How to Combat Global Warming

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Brief Summary

This is a science-based 396-page assessment of the best solutions to the problem of global warming. All agencies involved in the control of climate change agree that in addition to the reduction in emissions over the century it will also be necessary to remove hundreds of gigatons of CO_2 from the atmosphere. The methods to do this are called Negative Emission Technologies (NETs). Of the many varieties of NET, we conclude there are only six capable of sequestering CO_2 at a many hundred gigaton level. These are:

1. DACS. Direct Air Capture with underground Sequestration. While this is currently the most widely promoted and funded NET and is working well burying thousands and possibly millions of tons CO_2 , we point out multiple technical and safety problems (p 23-26) involving the danger of deadly leaks when hundreds of gigatons of CO_2 need to be buried. The following alternatives are needed.

2. *In situ. In situ* Underground Mineralization eliminates the safety issue but is still costly and at the multiple gigaton level, has issues with the raising of ground levels. Like DACS it does not address ocean acidification.

3. EW Enhanced Weathering. This NET uses ultramafic and mafic rocks (climate rocks) which combine with CO_2 and convert it to a permanently mineralized form. This is most effective if the ultramafic rocks (olivine and others) are ground to 1 um size, a process that can be powered by renewable solar and wind energy. With EW the mineralized CO_2 is safely stored **above ground**, eliminating the dangers of the burial of many gigatons of CO_2 gas.

4. OAE Ocean Alkalinity Enhancement. Initially this involved the use of finely ground ultramafic rocks such as olivine. However, computer modeling has suggested that olivine was not nearly as effective and safe as CaO, MgO and Mg(OH)₂. CaO and MgO can be obtained from tailings and Mg(OH)₂ can be generated in large quantity from olivine.

5. eOAE Electrolysis assisted OAE that uses olivine plus electrolysis to accelerate the process and improve its efficiency.

Activating EW, OAE and eOAE all require an international effort at mining and processing gigatons of olivine or other climate rocks.

6. heOAE hybrid electrolysis OAE. This is an eOAE that does not require the use olivine or other ultramafic rocks. It utilizes a hybrid of two electrolysis techniques. It a) directly removes CO₂ from seawater and converts it to carbonates which permanently store CO₂ in the ocean and b) alkalinizes the seawater that is returned to the ocean allowing it correct for ocean acidification and to absorb more atmospheric CO₂. To distinguish it from eOAE using climate rocks, it is termed it heOAE. This is an ideal NET in that it does not involve burying gigatons of CO₂ gas and does not require mining and processing gigatons of olivine and does not require adding any foreign substances to the ocean.

(Continued on the overleaf)

However, it does require large amounts of electricity which can be supplied by hydrogen fuel cells and mid-ocean floating solar and wind turbine farms and OTEC (Ocean Thermal Energy Conversion).

We propose that EW, OAE, eOAE and heOAE can satisfy the following conditions:

- 1. Capable of permanently sequestering many gigatons of CO₂ each year.
- 2. Storage is safely above ground or in the ocean.
- 3. EW improves rather the removes cropland.
- 4. Combats ocean acidification, deoxygenation and warming.
- 5. Combats land and ocean release of N_2O and CO_2 .

Before EW, OAE and eOAE can be activated it will be necessary for the U.S. and all other countries to begin mining and grinding gigaton quantities of olivine and other climate rocks.

We conclude that EW, OAE, eOAE and heOAE are critically needed additions to DACS if we have any hope of controlling global warming by removing hundreds of gigatons of CO₂ from the atmosphere. One additional advantage of EW is that the drone program described allows individual citizens to participate in the removal of CO₂ from the atmosphere. Catamarans carrying heOAE technology also have the potential of providing a method for individual climate activists to participate in the removal of CO₂.

This review is rich with ideas that even if only some of them were carried out to completion could result in the safe sequestration of gigatons of CO_2 each year and go a long way toward halting global warming. But most of them cannot even start until we begin mining climate rocks in the U.S. and the rest of the world. Funding of EW and the three OAEs is critically needed. Since all branches of the military are committed to help fight global warming (a new kind of war) some of this funding and operating could be done through the different branches of the defense department. The way in which the different branches of the government can be involved as reviewed in the Addendum.

Given the potential restrictions on government spending - philanthropists, billionaires, NGOs, and non-profits will increasingly be relied on to combat global warming by both supporting efforts to reach net-zero emissions and by removing CO₂ from the atmosphere.

And - we must start NOW!

Digital copies of this document and its Addendum can be downloaded at www.thecomingsfoundation.org

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A Review and Proposals

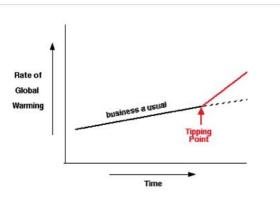
Summary

In this document, to aid in reading the critical points will be in **bold**. The super-critical points will be in **<u>underlined bold</u>**.

This document is a science-based assessment of the best solutions to the problem of global warming. All agencies involved in the control of global warming concur that simply cutting down on emissions will not be enough. In fact, the current level of atmospheric CO₂ is 420 ppm, significantly more than at the time of the first climate conference. There is wide agreement that the emission proposals at COP26-28 will not keep the earth's temperature below 1.5°C (Masood and Tollefson (2021). Some suggest that the battle for avoiding a 1.5°C level has already been lost (Hanley, 2022).

Rogelj et al (2023) published an article entitled, *Credibility gap in net-zero climate targets leaves world at high risk*. This was a report that looked at policies instead of promises. It showed that global climate targets may be missed by a large margin. Clearly, something must change, and it must change quickly. This document examines what those changes could be.

The planet is also moving "**perilously close to tipping points that could lead to avalanche-like cascading and irreversible climate impacts.**" (IPCC 2022). A tipping point for global warming is a temperature at which events begin to happen that produce **a positive feedback loop**, rapidly accelerating further temperature rise above the previous rate. The following figure illustrates the effect of tipping points.



Tipping points are already upon us and are potentially very catastrophic. Many tipping points have been identified for climate change (Fabbri, et al 2021; McKey et al 2022). They are all scary, but the following are some that are especially scary.

1. *Plants switch from photosynthesis to respiration.* As global temperatures increase a point is reached at which all plants on earth begin to switch from predominately photosynthesis (consuming CO_2 and producing oxygen), to respiration (consuming oxygen and producing CO_2). Duffy et al, (2021) state that at the current rate of temperature rise this process will be well underway by 2040 and in some places, it is already occurring.

2. *Melting permafrost.* The Arctic is warming four times faster than the rest of the world (ICCI 2022). We are currently at a temperature at which the vast amounts of permafrost begin to melt with the release of huge amounts of methane, a greenhouse gas that is 80 times more potent than CO₂. This has already started in parts of Siberia (Shakhova, *et al.* 2010; Welch (2019); Kindy, 2021) and the North American arctic. **Deep melting of the permafrost with the formation of sink holes has also already started.**

3. *Melting methane hydrates.* It is estimated the up to **12,000 billion tons of carbon is present in methane clathrates** on the sea floor at 300 to 600 meters, **comparable to the total amount of carbon in all fossil fuels**. The **gas hydrate dissociation hypothesis** suggests that part of the 41 to 45 °F rise in global temperatures during the **Paleocene-Eocene Thermal Maximum** was due to a methane burp from melting of methane hydrates. It could happen again.

4. *Loss of albedo.* The ice in the arctic, Greenland and the Antarctic reflect large amounts of solar radiation back into space, cooling the planet. The accelerated melting of this ice destroys this albedo effect (Riihelä, et al (2021). This melting also causes an increase in sea level with the displacement of hundreds of millions of people (NIC-NIE, 2021). Climate change skeptics have seized upon the fact that in some places in Antarctica sea ice is expanding. This varies from year to year and is a tiny proportion of the total Antarctic ice. The pair of GRACE satellites that actually weigh the mass of the ice show that **billions of tons of ice are melting at both poles**.

5. Die off of phytoplankton. It is rarely appreciated that phytoplankton in the ocean sequesters as much CO_2 as all the trees on land (Longhurst, et al 1995; Field, et al, 1998; MacRae, 2020). If these die off because of ocean acidification, warming, and deoxygenation which is progressing at a rapid rate, this huge reservoir of carbon dioxide sequestration will be lost. In addition, phytoplankton are at the bottom of the food chain for many animals including humans.

6. *Collapse of the AMOC*. A collapse of the Atlantic Meridional Overturning Circulation would alter the North Atlantic air temperatures by 7°C. The AMOC is a critical part of the Earth's Climate System that transfers warm water northward (to Europe) and deep cold water southward (NIC-NIE, 2021).

76. Collapse of the WAIS (West Antarctic Ice Sheet) Another scary tipping point was reviewed by Linden, (2022). The WAIS sits on bedrock and as such it is inherently unstable. If the amount of ice it sheds continues to exceed the amount it gains, it can set in motion a cascade of positive feedback that led to its collapse resulting in a 13-foot rise in sea levels.

8. Forest wildfires. As global temperatures and draughts increase, the risk of wildfires increases. This both increases atmospheric CO₂ levels and decreases the capacity of forests to store CO₂. Currently wildfires make up 5 to 10 percent of annual global CO₂ emissions each year. This is a tipping point that has already been in play for years. The month of July 2023 contained many days that were hotter than any recorded-on earth.

The occurrence on one tipping point can lead to a cascade of other tipping points. Tipping points add additional urgency the need to quickly stop the rise in the mean earth temperature past 1.5°C. Additional details about tipping points are given on pages 285 -295. The proposals outlined in this document provide pathways to halting this temperature rise despite the continued emissions of CO₂.

All agencies involved in the control of climate change agree that in addition to the reduction in emissions, it will also be necessary to remove hundreds of gigatons of CO_2 from the atmosphere. The methods to do this are called Negative Emission Technologies (NETs). Of the many varieties of NET, we conclude there are primarily six capable of sequestering CO_2 at gigaton levels. They are:

1. Direct Air Capture with underground Sequestration (DACS). While this is currently the most widely promoted and funded NET, we point out multiple problems, the most significant of which are cost and safety (pages 23-26). In addition, the IPCC states that the implementation of mechanical DAC along with underground sequestration of CO_2 "currently faces technological, economic, institutional, ecological-environmental and socio-cultural barriers."

2. *In situ* mineralization eliminates the safety issue but is still costly and has issues with elevation of the land above injection sites.

3. Enhanced Weathering (EW) This requires the use of ultramafic and mafic rocks. We term them climate rocks. For their most effective use they need to be ground to 1 um size, a process that can be powered by solar/wind energy. EW is safe because the CO₂ is stored in mineralized form above ground.

4. Ocean Alkalinity Enhancement (OAE). This also involves the use of finely ground ultramafic rocks. However, computer modeling indicates that olivine is not nearly as effective and safe for OAE as CaO, MgO and Mg(OH)₂. The later can be generated in large quantity from olivine. Thus, activating OAE will also require mining and processing gigatons of olivine worldwide.

5. Electrolysis assisted OAE which we have termed **eOAE**. It uses olivine and other ultramafic rocks and electricity to assist their dissolution.

6. heOAE: Hybrid electrolysis OAE uses a hybrid of two electrolysis processes. One removes CO_2 directly from seawater and converts it to carbonates which permanently stores CO_2 in the ocean and the other alkalinizes the returning sea water to provide ocean alkalinization enhancement.

<u>heOAE is an ideal proposed NET in that it does not involve burying gigatons of</u> <u>CO₂ gas and does not require mining and processing gigatons of olivine or other minerals.</u> Ideally, heOAE can be placed on boats such as catamarans or ships such as barges. If those vessels utilize renewable energy, once they are paid for, they can <u>continue to</u> <u>sequester CO₂ for many years at a low cost.</u>

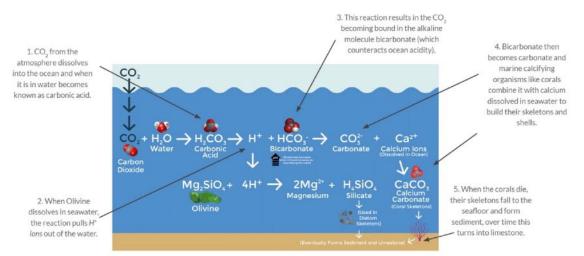
The Equation that Once Saved Planet Earth – It Can Do It Again.

The atmosphere of Venus is 96.5% carbon dioxide resulting in a deadly temperature of 872 °F. By comparison, the atmosphere of the earth contains 0.04% CO₂ and has a temperature which is compatible with life. Schuiling (2013) pointed out that the difference between the two planets was the presence of water on earth which allowed the CO₂ to be permanently mineralized. It was based on the following equation where the left-hand compound is olivine, an ultramafic rock.

 $(Mg, Fe)_2SiO_{4(s)} + 4H_2O_{(l)} + 4CO_{2(g)} \leftrightarrow 2(Mg^{2+}, Fe^{2+})_{(aq)}$ $+4HCO_3^{-}(aq) + H_4SiO_{4(aq)}$

In this reaction, sequestering CO₂ could only occur in the presence of water (H₂O).

Mafic rocks such a basalt, are rich in magnesium (ma) and iron (fic) and silicates. **Ultramafic** rocks such as olivine and dunite have lower amounts of silicates. **Serpentines** are hydrated forms of ultramafic rocks.



The fate of the different parts of the above equation are shown below.

Figure from Project Vesta

 CO_2 from the atmosphere dissolves in water producing carbonic acid, H₂CO₃, which produces acid H⁺ and HCO₃⁻ and acidifies the ocean. Ultramafic minerals such as olivine, Mg₂SiO₄, combine with the H⁺ to produce silicates which are taken up by diatoms which die and fall to the ocean floor. The carbonic acid also produces carbonates, CO_3^{2+} , which combine with calcium Ca²⁺ and Mg²⁺ to produce calcium carbonate, CaCO₃, which is used by corals and shells of other marine organisms, and Mg carbonate which also permanently stores CO₂. Combined, these and other reactions **permanently store in mineral form 99.94% of all the CO₂ ever produced on earth and make the earth a livable planet.**

This equation saved the planet earth once and it can, with our help, save it again.

What is meant by, "With our help?" The speed of the above equation can be dramatically increased by grinding the rocks to a fine powder (1 um or less) and spreading them on croplands, non-croplands, and the ocean. One of the reasons the NETs will be critical is that to date attempts to reduce emissions alone are not working fast enough. The US Military has identified the worldwide disruptions due to Climate Change as **one of the greatest threats to US security**.

In this review we show that the above equation in its accelerated form can be utilized in NETs called **Enhanced Weathering (EW)**, **OAE** and electrolysis assisted **Ocean Alkalinity Enhancement (eOAE and a hybrid form of electrolysis assisted OAE - heOAE)**.

Devastation Caused by Global Warming is here now. The level of CO₂ in the atmosphere continues to rise. Weather related disasters around the world led to \$3 trillion in losses between 2010 and 2019 (Linden, 2022). Firestorms are ravaging the western US and other countries such as Canada, Greece, Russia, Australia and Chile the rate of melting of ice in Greenland, the Arctic and Antarctic is rapidly increasing, sea levels are rising and threatening cities, draughts and accompanying crop failures are increasing worldwide with widespread starvation and refuge migration, the temperature of both the air and water are rising, we are losing island nations such as Tuvolu, the warm waters are causing more violent hurricanes and tropical storms resulting in billions of dollars of destruction, the **permafrost** which holds trillions of tons of methane and organic carbon is thawing, glaciers and snow fields which supply 75% of the world's fresh water for drinking and irrigation are rapidly melting, water reservoirs are at an all-time low and in some places result in loss of hydroelectric electricity, electric automobiles still represent a small fraction of all cars, and renewable energy still represents a minor percent of total electricity production. In addition, the acidification of the oceans is threating the food supply for billions of people. And, if you think this is bad, read David Wallace-Wells (2020) account what the world will soon be like if we do not get emissions and global warming under control. Sliding past 1.5°C and into 2°C and higher by 2040 and 2050 portends a horrific world with 150 million people dying of air pollution and heat, 200 million climate refugees and many trillions of dollars in mitigation efforts. Independent of what could happen, Sognnaes, et al (2021) reported that using seven diverse integrated assessment models the most optimistic scenario for reducing emissions is still insufficient to limit global warming to 2°C. The 2023 5th National Climate Assessment stated that all regions of the U.S. are currently being significantly affected by climate change.

The *in-situ* storage of CO_2 using large underground deposits of climate rocks can store trillions of tons of CO_2 by mineralization. These large deposits are in Oman, New Caledonia, New Guinea, and some are in the U.S. We need to identify these sites and use them for storing multiple megatons and even gigatons of CO_2 . This is far safer than storing CO_2 under basalt domes and other places because the CO_2 chemically and permanently binds to the climate rocks. It cannot be released by earthquakes or other accidents. However, the process of CO_2 capture is slow, energy intensive, there are mechanical problems with the great bulk of these injections.

Ultramafic rocks have the most carbon sequestration capability by mass and the fastest dissolution rates among silicate rocks, and thus are a prime candidate for enhanced weathering. When these silicate rocks erode, Mg and Ca form free cations that spontaneously bind CO₂ to form carbonate rocks (e.g., CaCO₃, MgCO₃). They are common, and deposits are present in most countries. When crushed to a powder they take up CO₂ and convert it to carbonates which store carbon for thousands of years. When placed in the ocean they bind up H+, add cations such as Mg⁺⁺ and Ca⁺⁺, increase alkalinity and decrease the acidity of the seawater. These NETs require no new technology. If all countries pledged to both reduce emissions AND use these technically straight-forward methods to sequester a significant part of the OO₂ they currently emit, global warming would be significantly slowed

and reversed. This would also be uniquely fair, since the amount of CO_2 each country would be asked to sequester would be directly proportionate to the amount they emit. If they do not have deposits of these rocks, they can purchase them from those who do, thus providing a new industry.

EW and the OAEs have Economic Advantages Instead of Disadvantages.

For 30 years the countries of the world have pledged to decrease emissions and yet the level of CO_2 in the atmosphere continues to rise even faster. Why? Because until massive renewable energy and electric cars are in place it is economically and politically costly to significantly reduce emissions. Until recently, the U.S. the congress has been notoriously slow and politically divided on efforts to combat climate change.

By contrast, **one of the over whelming advantages of the EW and the OAEs is that they come with an economic advantage rather than a penalty**. When you ask a country to cut emissions toward zero that is equivalent to asking them to significantly cut down on their energy supply - something that can be both economically and politically disastrous leading to resistance. In contrast, when you ask a country to start using EW and the OAEs it comes with economic advantages such as improved crop yields, reduction in soil acidity, reduction in soil erosion, expanded land suitable for agriculture, protection of fisheries and corals by combating ocean acidification and combating global warming by sequestering CO₂ and decreasing N₂O production on land and in the sea. In addition, the mining industries of that country would become very profitable and if the country could produce more of these rocks than they needed internally, they would enjoy an economic boon by selling the excess to other countries. This could be "the new oil." This plan would also open new jobs, worldwide. As a commodity it would easily pass ESG (Environmental Social Government) standards of investment.

We conclude the following about EW, OAE, eOAE and heOAE.

- by eliciting the cooperation of all countries to mine, grind, spread and use their mafic and ultramafic rocks for EW on croplands, non-croplands, and the ocean to sequester CO₂,
- by emphasizing the economic advantages of EW and the three OAEs,
- by utilizing heOAE that does not use ultramafic rocks or require burying CO₂.
- by grinding the rocks to a particle size of 1 um or less,
- by using carbon free sources of energy for grinding and for eOAE and heOAE,
- by using commercial waste sources of silicates (tailings),
- by factoring in the beneficial increases in crop yield,
- by factoring in the beneficial increase in pH of the soil,
- by factoring in the improvement of poor soils (oxisols and ultisols),
- by decreasing CO₂ emissions from soils and the ocean,
- by decreasing N₂O emissions from soils and the ocean,
- by increasing ocean alkalinization,
- by decreasing ocean acidification,
- by decreasing ocean warming,
- by decreasing ocean deoxygenation,
- by decreasing ocean warm "blobs",
- by emphasizing the use of EW at weathering "hot spots",
- by utilizing vertical "farming" to produce "hot spots" anywhere,

- by using carbon negative ships for OAE, eOAE and heOAE,
- by focusing OAE, eOAE and heOAE efforts on areas of CO₂ outgassing and threatened coral,
- by emphasizing the economic advantages to the miners of this "new oil,"
- by emphasizing to fossil fuel companies, the advantages of this "new oil"
- by surpassing ESG standards for commodity investing,
- by emphasizing the new jobs created world-wide,

• by partnering with New Caledonia to open their vast reserves of ultramafic rocks for both *in situ* and *ex situ* sequestration,

• by identifying large underground deposits of climate rocks and using them for *in situ* CO₂ storge in the U.S.,

• by urging the U.S. Military and Army Engineering Corp to start a project to mine, process and stockpile mafic and ultramafic rocks at the Twin Sisters

site in WA and other sites in the US,

• by devoting these rocks entirely to EW and OAE,

• by partnering with other government agencies such as the Department of Energy, Department of Defense, Army Corp of Engineering's Climate Preparedness and Resilience Program, US Navy, Department of Agriculture, Department of Commerce, CIA, Secretary of State, U.S. Geological Service, Department of the Interior, NOAA, NOAA OAP,

EPA, the Biden Climate Group, and others.

• by setting up a Drone Program whereby individual citizens in the hundreds of non-profit climate clubs and NGOs could spread pulverized climate rocks on vast areas of the U.S. and worldwide.

 \Rightarrow we could safely sequester multiple gigatons of CO₂ each yr.

Proposed Programs

1. Develop Blueprints for zero carbon eOAE ships USING OLIVINE and support their construction and use, and/or advocate for the Navy and NOAA to carry this out.

2. Develop Blueprints for zero carbon ships NOT USING OLIVINE (heOAE) and support their construction and use, and/or advocate for the Navy and NOAA to carry this out.

3. Advocate for the Government to Develop Large-Scale Mining and Grinding of Olivine at Twin Peaks, WA, and other sites.

4. Advocate for the Global Cooperation for EW by mining, processing, and using ultramafics climate to sequester CO₂.

The major energy cost of EW is that involved in the grinding of the rocks. A source of renewable, carbon free electricity for grinding may require solar or wind farms, or the utilization of modular Molten Salt Nuclear Reactors or the U.S. Military's Deployment of Microreactors. The U.S. Military and the Army Corp of Engineering are uniquely suited to carrying out this project and working with these sources of energy.

Another Economic Advantage of EW, OAE, eOAE and heOAE. An additional significant advantage of the EW, OAE, eOAE and heOAE approach is that they would save trillions of dollars in mitigation costs. If the CO_2 sequestration was spread among all countries of the world the US would only need to sequester the amount of CO_2 equal to its own emissions. Goff and Lackner (1998) pointed out we have more than enough ultramafic rocks in the U.S. to do that. A U.S. Navy based fleet of OAE, eOAE and heOAE ships would also contribute greatly to the safe sequestration of CO_2 .

We need to remove CO_2 from the atmosphere for centuries. When and if we approach zero emissions, some of the CO_2 currently in the atmosphere will still be there for thousands of years. By 2035-2045 the level of atmospheric CO_2 will probably be in the range of 440 to 500 ppm. This level will still be causing wide-spread and very serious problems.

University of Chicago oceanographer David Archer has stated that, "The climatic impacts of releasing fossil fuel CO_2 to the atmosphere will last longer than Stonehenge, longer than time capsules, longer than nuclear waste, far longer than the age of human civilization so far. For all practical purposes, it never goes away. Each ton of coal that we burn leaves CO_2 gas in the atmosphere. The CO_2 coming from a quarter of that ton will still be affecting the climate one thousand years from now." (SkS, 2017).

To make these problems go away it will be necessary to continuously remove gigatons of CO₂ from the atmosphere for centuries. This also applies to combating ocean acidification, deoxygenation and warming. Some of the billions of dollars that are currently committed for mitigation in the Green Climate Fund, and in the Inflation Reduction Act could be used to jump start these operations. Non-partisan support of these efforts is critical. Ship based heOAE using renewable energy is uniquely suited for combating global warming over the long term.

What Can Individuals Do? There are many hundreds of non-government and nonprofit organizations worldwide devoted to combating global warming with many thousands of members. There are also many individuals with the means to help but lack specific plans. These people are looking for something they personally could do that could really make a difference. We propose ways in which such individuals can play a direct role in the removal of CO_2 from the atmosphere.

1. The development of a **Drone Program** whereby these volunteers could purchase inexpensive drones designed to spread pesticides or seeds on croplands. These could be used to spread a slurry of finely ground climate rocks over huge areas of the country including mountains, forests, grasslands, scrub lands, marshlands, and other areas. This program could also spread the rocks on croplands, relieving the farmers of this task.

Such a program can allow millions of individual concerned citizens world-wide, to actively participate in the removal of CO_2 from the atmosphere. As the devastating effects of global warming begin to directly affect everyone, I believe huge numbers of individuals would like to participate. **Our youth are especially involved** three ways: a) they are the most vocal and active of the climate activists, b) they have the most to lose if we don't get global warming under control, and c) the are more tech savvy than most adults.

Drones are cheap and affordable. In a similar vein, over 20 million families in the U.S. had victory gardens to help with WWII. I believe that worldwide an even larger number of individuals will be motivated to help to fight this new, and potentially more deadly, World War III. Coordination of these efforts will be needed at the city, county, and

state level. The national government's role would be that of general oversight and to ensure a steady supply of price subsidized, pulverized climate rocks.

2. Develop a ship based **heOAE Program**. Research is needed to determine if relatively inexpensive and safe ships can be designed to carry out heOAE using carbon free energy. If possible, many countries, philanthropists, billionaires, NGOs, non-profits and even individuals could purchase and sail them. This could provide a huge fleet of such ships contributing significantly to the long-term removal of CO_2 from the ocean and atmosphere. It would supplement the development by the U.S. Navy of nuclear powered eOAE/heOAE ships.

3. Advocate for governments, philanthropists, billionaires, NGOs, and non-profits to support the use of EW, OAE, eOAE and heOAE.

Government Subsidies. The U.S. Government has spent billions over the years in subsidies for the fossil fuel industry. As the with the use of fossil fuels, the government should instead be **subsidizing a climate rocks and EW, OAE/eOAE/heOAE industry**. This could keep the price of ground climate rocks and ships at a level that these non-profits and others could afford them. In addition, the fossil fuel companies could switch from removing oil from the ground to removing climate rocks from the ground.

The Addendum. We have added an addendum entitled, *How the Different Parts of the U.S. Government and Private Sector Can Help with Enhanced Weathering, OAE, eOAE and heOAE to Rapidly Combat Global Warming*. It summarizes this document and outlines suggestions on how the many different branches of the US government, NPOs and many nonprofit climate clubs could help to accelerate the adoption of EW, OAE, eOAE and heOAE.

In Summary EW, OAE, eOAE and heOAE serve as important adjuncts to the different approaches to combating climate change and global warming. They are the only NETs that can satisfy all the following issues.

- 1. Capable of sequestering/storage of many gigatons of CO₂ each year.
- 2. The sequestering is safe and permanent.
- 3. Storage is above ground or in the ocean, avoiding problems of below ground storge.
- 4. EW improves rather than removes cropland.
- 5. OAE/eOAE/heOAE combats ocean acidification, deoxygenation and warming.
- 6. Combats land and ocean release of N₂O and CO₂.
- 7. EW does not require an energy intensive step to release CO₂, as with DACS and *in situ*.
- 8. At gigaton levels of sequestration/storage it is safer than DACS.
- 9. EW provides a method in which climate clubs, climate activists, and ordinary citizens, through the Drone Program, can play an active role in the safe removal of CO₂ from the atmosphere. This is in dramatic contrast to DACS that is performed by only a few companies with huge, expensive instillations.
- 10. In marked contrast to other NETs, once heOAE ships running on renewable energy are built and paid for, the ongoing, long-term extraction of CO₂ from the ocean and atmosphere would be very inexpensive, saving many billions to trillions of dollars.

The Logic Tree

- 1. It is universally agreed that it will be necessary to remove CO₂ from the atmosphere as well as reduce emissions.
- 2. Of the numerous NETs only EW/OAE/eOAE/heOAE satisfy the above issues.
- 3. Gigatons of climate rocks will be required to carry out EW/OAE/eOAE at scale.
- 4. Many countries of the world need to begin mining and grinding their deposits of climate rocks and using them for EW/OAE/eOAE.
- 5. This will require leadership from the USA government and the UN.
- 6. Development of heOAE worldwide could decrease the need to mine huge amounts of climate rocks and avoid the danger of burying gigatons of CO₂.

7. The retrofitting of the U.S. Navies fleet of its nuclear-powered ships with heOAE technology would provide a powerful start to the sequestration of multiple megatons of CO_2/yr .

In the book *All We Can Save*, Naomi Klein stated, "Young people around the world are cracking open the heart of the climate crisis, speaking of a deep longing for a future they thought they had but that is disappearing each day that **the adults fail to act on the reality that we are in an emergency.**"

Unless countries step up their efforts to cut greenhouse gas emissions, the planet will on average be 2.4 to 3.5 °C warmer by the end of the century. And the results will be catastrophic. Antonio Guterres UN Secretary General & IPCC 2022

"...Increased action must begin this year, not next year, this month, not next month, and indeed today, not tomorrow." Inger Andesen Executive Director UN Environment Program

"We need a whole new way of thinking." Greta Thunberg

How to Combat Global Warming

Dr. David Comings

The Comings Foundation A Non-profit Foundation Devoted to Fighting Global Warming

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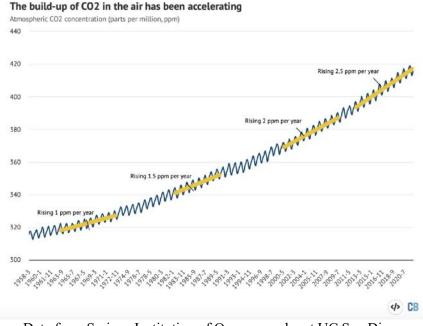
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How to Combat Global Warming Dr David Comings The Comings Foundation <u>www.thecomingsfoundation.org</u> A Non-profit Foundation Devoted to Fighting Global Warming

Keeling, Mauna Loa Observatory, and COPs To date the primary method of combating global warming is through a series of Conference of Principals (COP) meetings at which the countries of the world commit to reducing their CO₂ emissions. The last of the series was COP27 in 2021 in Sham el-Sheikh. So how is this working? In 1958 David Keeling set up the Mauna Loa Observatory in Hawaii, at 11,140 feet above sea level, to monitor atmospheric CO₂ levels (Keeling et al, 1995, Harris, 2010) The results of these readings is shown below.



Data from Scripps Institution of Oceanography at UC San Diego. Chart by Joe Goodman for Carbon Brief

The rate by which the levels of CO₂ are increasing were **1 ppm/year in 1997** at the time of the Kyoto COP, to **1.5 ppm/year ten years later in 1987**, to **2 ppm/year 10 years** after that, to **2.5 ppm/year currently**. At that time of the Kyoto COP the level of CO₂ was approximately 365 parts per million. The current level is 420 ppm. The levels of CO₂ are increasing instead of decreasing and the rate of the increase is increasing, not decreasing as was hoped.

Based on these and other findings, all the premier organizations dedicated to combating climate change have concluded that in addition to reducing CO₂ emissions it will be necessary to also remove (sequester) CO₂ from the atmosphere to avoid an excessive rise in the earth's temperature (NAS 2015). For example, the 2019 Intergovernmental Panel on Climate Change (IPCC, 2019) Special Report on Global Warming of 1.5°C (SR1.5) outlined the importance of reaching net-zero emissions by 2050 to limit warming to 1.5 degrees. They also recommended

CDR (Carbon Dioxide Removal) and suggested it be at a 10 gigatons per year level. The **National Academies of Science (NSA) estimated that 10 billion metric tons (gigatons, or Gt)** of CDR per year would be required globally by 2050 and up to 20 Gt per year by the end of the century. (NAS 2019 p9).

The 2021 UN Report on Climate Change is scary. However, the most extensive report yet of the devastating effects of climate change are in the 3,650-page IPCC Climate Change (2022) Impacts, Adaption and Vulnerability Working Group II.

CDR (Carbon Dioxide Removal) is not meant to minimize the need to cut emissions. Both approaches are critically needed. Neither will do the job alone. The concepts involved are called **Negative Emission Technologies or NETs**. Various NETs have been proposed but so far but only a few have developed beyond the laboratory and there is yet little public funding for most of them (Bach et al, 2019).

That is where private foundations come in. They can support some of the research, development, and implementation of the most promising technologies – Enhanced Weathering on Croplands and Non-croplands (EW), Ocean Alkalinity Enhancement (OAE) using CaO, MgO or Mg(OH)2, eOAE using olivine augmented with electrolysis, and heOAE involving hybrid electrolytic extraction of CO_2 directly from seawater with the formation of carbonates, and alkalinization of the effluent without using olivine.

Negative Effects of ISDS. An additional problem affecting the attempts to reduce levels of atmospheric CO_2 is the negative effect of Investor-State Dispute Settlements (ISDS). This is a system through which investors can sue countries for discriminatory practices, such as reductions of emissions, that effect their investments. An example is the Canadian firm, TC energy is suing the U.S. government for \$15 billion to compensate them for the cancellation of the Keystone XL Pipeline. Such cases have exploded in recent years. This can obviously counteract the Paris agreement efforts to curb emissions (Tiehnaara et. al. 2022). ISDS enhances the need to have countries also commit to sequestering CO_2 from the atmosphere since sequestering CO_2 would be largely immune to ISDS claims.

CCS, CCUS, DACS. One of the most common NET proposals is **Carbon Capture and Storage (CCS)**. This involves the capture of CO_2 **emitted by power plants burning fossil fuels**. This capture is followed by the sequestration of the CO_2 into various underground storage sites. A modification of this approach is **CCUS (Carbon Capture Use and Storge)** where the captured CO_2 is put to a variety of uses and the excess sequestered. For an extensive review of the many potential uses of CO_2 see Mikkelsen, et al (2010) and Olajire (2013). Currently, the most widely supported NET is **Direct Air Capture with Sequestration (DACS)** with underground storage (Keith et al 2018).

Problems with underground storage.

First, there have been many CCS plans that involve sequestration of the CO_2 from coal powered plants. However, if the carbon capture is limited to the output from power plants, that will only mitigate emissions and not reduce the total amount of CO_2 in the atmosphere.

A 2021 GAO report showed that CCS plans have largely failed. Since 2009, the Department of Energy has invested \$1.1 billion on 11 projects to show how carbon dioxide emissions from coal-power and industrial facilities could be captured and stored. DOE initially committed to 8 coal projects, mostly new power plants with carbon-capture equipment. DOE provided nearly \$684 million to eight coal projects, resulting in one operational facility. Senior management directed DOE to bypass some cost controls to help struggling coal projects. As a result, DOE spent almost \$300 million more than planned on 4 facilities that were never built.

As of 2023 there were 18 DACS plants removing collectively 11,000 tons of CO_2 . The DOE allocated \$1.2 billion for 2 hubs in Texas and hoped to create 4 hubs in the next ten years each capable of removing one million tons of CO_2 (Brainard, 2023). That is $1/250^{\text{th}}$ of one gigaton and $1/2,500^{\text{th}}$ of 10 gigatons. Hardly the solution the NAS was recommending.

In early 2024 the European Commission presented its goal of cutting greenhouse emissions 90% by 2040. In addition to reduced emissions, carbon dioxide capture and sequestration was proposed to allow them to reach this stringent goal. Richard Klein of the Stockholm Environment Institute stated, "But it simply hasn't been shown to work at the scale that would be needed – it remains a pipe dream."(Sanderson and Wong, 2024).

We would recommend that in both the U.S. and EU, the money being spent on DACS would be better spent supporting EW, OAE, eOAE and heOAE.

Second, the DACS process has considerable energy requirements and financial costs (Siefert and Litster, 2013; Lebling, et al. 2022). Encouragingly, some variations are less energy intensive (Chen et al, 2023, Kim et al 2023).

Third, there are serious concerns about the permanence and safety of the sequestered CO_2 due to earthquakes and other factors (Yu et al, 2008; Gough, 2008; Kirchsteiger, (2008); Newmark et al (2010); Oltra et al 2012). There are also potential problems with corrosion and leakage of CO_2 pipelines (Mazzoldi et al, 2008). Xie et al (2015) stated that,

"Public perception concerning CO_2 storage in the geosphere is generally negative due to the perceived risks of leakage and geologic disasters" (Herzog et al. 2013; Park et al. 2012; Schutze et al. 2012). See **Tenth** (below), for further discussion of leakage. Oglesby (2023) also reviewed many of the short comings of DACS.

Fourth, in a *Nature Climate Change* article entitled, "Uncertain storage prospects create a conundrum for carbon capture and storage ambitions" Lane et al (2021) suggest, "... it's the rate at which CO₂ can be safely injected and permanently contained that counts."

Fifth, regarding CCUS MacDowell et al (2017) point out that it is highly improbable that chemical conversion of CO_2 to other products will account for more than 1% of the mitigation challenge.

Sixth, as pointed out by Mann (2021) a common place for sequestering the CO₂ recovered from power plants is oil wells, i.e., **Enhanced Oil Recovery (EOR)**. He stated that the recovered oil, when burned, would yield several times as much CO₂ as was sequestered in the first place. Also, this process is only about 90% effective in removing the CO₂ produced, leaving millions of tons still being released.

Namoi Oreskes (2024) also expressed considerable doubt about CCS (DACS) and EOR where the CO₂ is used for tax credits for the oil industry and for EOR. In an article entitled *The False Promise of Carbon Capture*, she was concerned about two aspects of this approach. First, in contrast to my concern about massive leaks (see below) she was concerned about slow leaks, stating that "the mechanism for ensuring that the CO₂ is not leaking back into the atmosphere are flimsy at best." Second, like Mann, she was concerned this this would further increase the use of fossil fuels. Finally, she stated that, "while it [carbon capture and storage] might be part of the solution down the road, right now **it is mostly a dangerous distraction**."

Seventh, a study by Bartholomew and Mauter (2021) points out that one of the major proposed sites for sequestering CO₂ are the **large salt reservoirs underneath basalt domes**, and here one problem is cost. The brine in these reservoirs is **three times more concentrated than seawater**. These brines will either need to be disposed of via deep well injection or desalinated for beneficial reuse. Pumping it underground—an approach that has been used for oil and gas industry wastewater—has been linked to increased earthquake frequency and has led to significant public backlash. **Desalinating the brines is costly and energy intensive** due, in part, to the efficiency limits of desalination technologies.

Eighth, Jahediesfanjani, H. et al (2018) reported that the most likely scenario for underground CO₂ storage involves **only injecting into those Storage Assessment Units (SAUs) with less than half of their area covered by actively produced conventional or unconventional hydrocarbon reservoirs.** There are only eight major such SAUs. These have a total CO₂ injection and storage capacity of less than 300 Mt/year (.3 Gt/year). **This is insufficient to handle the Beyond 2 Degrees Scenario (B2DS)** recommended by the 2015 Paris Climate Conference.

Ninth, Conversion of CO₂ to methane with storage of CO₂ in depleted oil wells is an additional complication of CCS, namely 13 to 19% of the CO₂ injected into depleted oil wells is converted to methane by methanogenic bacteria as follows:

 $CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O$

Methane is more mobile than CO_2 and therefore there is an enhanced risk of escaping gas. In addition, up to 74% of injected CO_2 is dissolved in ground water, a further source of loss (Tyne, et al, 2021). Thus, of the two major proposed sites of storage in carbon capture and storage, the basalt domes have problems with high levels of salinity and the depleted oil wells have problems with CO_2 loss by conversion to methane and solubility in ground water. CCS and CCUS is not as simple and straight forward as it may appear.

Tenth, The Danger of Leakage. To combat global warming in time to avoid many trillions of dollars of damage to the world and many deaths, will require the yearly removal of 10 to 20 gigatons of CO_2 from the atmosphere (NAS 2019). The NET that is currently the most popular is Direct Air Capture with Sequestration (DACS). This utilizes chemical methods such as those of Climeworks and Carbon Engineering. The captured CO_2 is then stored underground, such as under domes of basalt or under sedimentary rocks or into old oil wells. The U.S. Department of Energy has committed 3.5 billion dollars for multiple hubs testing this approach.

With considerable effort DACS can work at megaton levels. However, the situation changes dramatically at the 10 - 20 gigaton/yr level. At this level, DACS is both expensive and potentially dangerous. It is expensive because removal of the captured CO₂ is very energy intensive. Dr. Arun Majumdar, founding Director of ARPA-E, pointed out that with the current machines removal of the captured CO₂ will require 2,000 - 2,500 kilowatt hours of carbon free energy per ton of CO₂, most of which is heat (U.S. Department of Energy's Carbon Negative Shot Summit (2022). Thus, **1 gigaton of CO₂ per year would require about 2,000 terawatt hours of carbon free sources. The entire US production of electricity is 4,000 terawatts, and that is for only 1 gigaton.** At 10 gigatons/year it would require five times the total electrical output of the U.S. Hopefully efforts to reduce this energy requirement will succeed.

Lake Nyos At this level of storage there is also a danger that a leak, earthquakes, or other accident could release megatons of CO₂ and kill many thousands of people. This is much more CO₂ than the thousands of tons of CO₂ released from Lake Nyos in Cameroon in 1986, that killed 1,746 people and over 3,500 cattle (Lake Nyos 2020 a, b). The dead cattle had no flies

because they were also dead. There were no birds singing because they too were dead. This was not some super rare Black Swan. The same thing happened two years earlier in nearby Lake Monoun killing 37 people. While the release of CO_2 from lakes and the release from storage are not the same, this episode illustrates what could occur with a large leak. This devastation was possible because **CO₂ is heavier than air and spreads over land like a carpet of death**. If this were to happen with DACS it could kill more people than those who have died in Chernobyl, Three-mile Island and Fukushima combined. Just as these events virtually put an end to the building of new nuclear reactors, a major release of CO_2 with many deaths would spell the end of DACS. Should this happen NETs, capable of safely storing gigatons of CO_2 above ground **need to be in place**. *In situ* sequestration (see below) is considered safe but still requires the same costly chemical methods of CO_2 capture. There are also problems with the deformation (elevation) at the injected sites. One need only to look at the mass of gigatons of CO_2 (page 253) to understand why this could be a problem.

Chlorine gas is also heavier than air and its devastating poisonous effects are well known following its use in the Ypres sector in WWI. There would be great concern and NIMBY objections if it was chlorine gas rather than CO₂ that was being buried. CO₂ seems so benign. It is in dry ice and all carbonated drinks. However, as Lake Nyos tells us, at levels of many tons of CO₂ release it can be just a dangerous as chlorine gas.

The proponents of DACS claim the deep underground sequestration of megatons of compressed CO₂ is safe. The success with DACS burying thousands of tons of CO₂ may have falsely led people into thinking it could work at multi-gigaton levels. To reach 1 gigaton would require 1,000 one megaton burials. At 10 gigatons this is 10,000 burials. Over a period of 10 years, it is 100,000 burials. The National Academies Study proposed the removal of 10 gigatons per year till mid-century and then 20 gigatons/year (NAP 2021). This would be a total of 1,260,000 one megaton burials by the end of the century. To think that none of these would ever leak is beyond rational belief. Why take the chance when there is an alternative that safely stores gigatons of CO₂ above ground or in the ocean in the permanently mineralized from of carbonates and silicates, i.e., Enhanced Weathering, OAE, eOAE and heOAE?

The assessment of risks of a leak, and other issues such as contamination of ground water, have also been reviewed elsewhere (Wilson et al, 2003; Ide et al, 2006; Damen, et al 2016; Zhang, Z. and Huisingh, D. 2016; Alcalde et al, 2018; Oyewole et al, 2023). Zhang, Z. and Huisingh, D. (2016) stated that "Potential CO₂ leakage may be the main barriers to the development of CO₂ geological storage." Alcalde et al, (2018) calculated that **98% of stored CO₂ will be retained for up to 10,000 years.** That sounds wonderful but when storing at a level of 1,000 gigatons, that is a **leakage rate of 20 gigatons, a massive amount**. The **EPA** is also so concerned that they have set up a **Vulnerability Evaluation Framework (VEF),** an analytical framework that identifies and offers approaches to evaluate the potential for a Geologic Sequestration project to experience CO₂ leakage and associated adverse impacts. They have especially voiced concerns about underground sources of drinking water.

Offshore oil drilling was supposed to be safe. However, BP's Deepwater Horizon oil spill released 200 million gallons of oil into the Gulf of Mexico with disastrous environmental effects. **NOAA's map of oil spill incidents of all types in the U.S. mainland and offshore is so densely packed the dots overlap**. The map shows that **despite the best laid plans for safety**, **accidents do occur**. While environmentally disastrous, at least oil spills do not kill everything in sight.

Others have also had questions about the long-term retention of CO_2 underground (Blackford et al., 2014; Monastery, 2013), the potential dangers of leakage CO_2 that may kill vegetation (Zhao et al., 2017), animals (Farrar et al., 1995) and people (Hill, 2000) and the ability of DACS to remove more than a fraction of the CO_2 that is needs to be removed (Ho, D. 2023).

Enhanced Weathering (EW) and Ocean Alkalinity Enhancement (OAE, eOAE, heOAE) avoid these concerns. With EW the CO_2 capture is accomplished in a single step that is exothermic, releasing rather that consuming energy (Schuiling, R.D. (2013). There is a cost of grinding the rocks but that can be supplied by renewable wind or solar or nuclear. Also, the captured CO_2 and the CO_2 sequestration is above ground, eliminating the potential problems with underground storage.

Mafic and ultramafic rocks are common, and deposits are present in most countries. One of the most effective is olivine. Its most common variety is a magnesium form, Mg_2SiO_4 called Forsterite. For EW The critical equation is:

$$Mg_2SiO_4 + 4CO_2 + 4H_2O => 2Mg_2^{++} 4HCO_3^{-} + H_4SiO_4$$

olivine + CO₂ + water = carbonates + silicates

These types of rocks are needed for EW, OAE and eOAE.

As outlined below, the combination of olivine and related minerals, $+ CO_2 +$ water is what saved the earth from being an oven like Venus. This equation and these rocks can once again save the earth from what humans are doing to it.

In nature, the above equation took place over thousands of years. This reaction takes place on the surface of the rocks. To maximize the rate of mineralization the rocks need to be **finely ground to a 1 um size. This can speed up the reaction to as little as several weeks or less** (see the following review).

Combating ocean acidification, warming and deoxygenation is also critical since **more than three billion people rely on the oceans for their livelihoods**. In addition, corals which are critical for the health of marine life, are currently dying, and the warm oceans are generating devastating hurricanes.

Removing CO_2 from the atmosphere is critical if we are to halt global warming and its destructive effects on our planet. This will be necessary even when or if we approach zero carbon man-made emissions because CO_2 remains in the atmosphere for up to a thousand years. In addition, gigatons of CO_2 are released into the atmosphere each year from both the land and the ocean and wildfires. This will require continued, long-term, safe sequestration of CO_2 .

There are currently over four hundred NGO and non-profit "climate clubs" worldwide with many thousands of climate activist passionate about controlling climate change and global warming (see addendum) They are largely limited to commitments to decreasing emissions and urging their governments to do more, more quickly. One unique advantage of EW is that these dedicated individuals can play an important role in spreading these climate rocks. It may also be possible to build catamarans or other ships that can carry out OAE, eOAE and heOAE and are cheap enough to be purchased by NGOs and climate change non-profits.

Oreskes (20220) also had many concerns about DACS and CCS and went so far as to claim there were **no current techniques capable of sequestering many gigatons of CO₂.** In contrast to this view, I suggest that EW, OAE, eOAE and heOAE are the ideal technologies for this purpose and may be **the only viable and safe methods of stopping global warming and**

reversing ocean acidification. These NETs would also be easier for underdeveloped countries to carry out. Currently, except for research, none of the limited amounts of mined ultramafic rocks anywhere in the world are used for EW/OAE or eOAE. As outlined in this document, we urge the rapid development of a global Manhattan type project involving the mining, processing, and utilization of these rocks for this purpose.

A More Optimistic Assessment about DACS has been published by Kivi, et al (2022). They developed a computer transport model to capture the dynamics of basin-wide upward CO_2 migration in a multi-layered setting over geological time scales. They found that massive capillary breakthrough and viscous flow of CO_2 , even though pervasively fractured caprocks, are **unlikely to occur and compromise the storage security**. Potential leakage from the injection reservoir is hampered by repetitive layering of overlying caprocks. This finding contributes to the development of climate policies around this technology with increased confidence that CO_2 will be indefinitely contained in the subsurface.

One might argue that direct monitoring of gigatons of stored CO₂ would provide a far safer assessment of the risks, than computer modeling.

DCCS, DAC, DACS refers to **Direct Carbon Capture and Storage (DCCS)** or **Direct Air Capture (DAC)** or **Direct Air Capture and Storage (DACS).** These approaches directly remove CO₂ from the atmosphere using one of several recent technologies such as Climeworks, Carbon Engineering, Global Thermostat, Lackner, and others. This has the advantage that the source of the CO₂ is virtually unlimited and equal to the total amount in the atmosphere and not tied to power plants. However, if it is stored under basalt domes or injected in oil wells, it has the **disadvantages as listed above** (pages 23-26) with concerns about the safety, permanence, and cost of the CO₂ storage. While proponents of CCS state it is safe, the long-term potential liability of the process may be placed on the taxpayers (Kusnetz, 2022).

A few projects using DAC with *in situ* chemical storage in basalt (a mafic rock), have started in Iceland and elsewhere, these involve the sequestration of thousands to millions of tons of CO₂.

In situ Storage by the injection of CO_2 directly into mafic and ultramafic rocks (see *in situ* sequestration below) is the safest form of underground storage for DAC because the CO_2 chemically and permanently binds to the rocks. A review of different aspects of this technique is presented below. Also see Ballerat-Busserolles, et. al. (2018). However, it also has a large energy cost to release the captured CO_2 and mechanical issues such as elevation of land at the injection site.

Department of Energy sponsored DAC At the COP26 Secretary Granholm announced the DOE Carbon Negative Shot initiative, part of President Biden's broader climate plan. This goal will span carbon removal solutions, from direct air capture (DAC) to carbon sequestration. The initiative aims to lower the cost of removal to \$100 per ton or less (for capture and storage), prioritizing high-quality lifecycle accounting, equity and justice, and durable storage for at least 100 years.

The DOE renamed the Office of Fossil Energy to include Carbon Management (FECM). The FECM leadership includes Dr. Jennifer Wilcox, Dr. Emily Grubert, and Dr. Shuchi Talati some of the best people Carbon 180 could imagine leading this program. However, many of the potential problems with underground storage are listed above. DAC plants use either a **solvent** or a **sorbent** technology. **Solvent plants** use a liquid solvent such as dilute potassium hydroxide to absorb CO_2 . The dissolved CO_2 then binds with calcium to form a stable solid mineral with the CO_2 then being released by the application of high-temperature heat (900°C/ 1,652°F), which is achieved with natural gas.

Sorbent plants use a solid sorbent which functions like a filter, selectively binding CO₂. They use low-temperature heat to release the CO₂ from the capture medium—80-120°C (176–248°F). This allows use of renewable energy and waste heat. They are built in a modular fashion with many smaller repeating units.

Both technologies require a great deal of energy. At 1 Gt scale (billion tons of CO₂) it would use around 8.8 percent of 2020's primary energy supply (Lebling et al, 2022; Keith, et al, 2018; Beuttler, et. al. 2019). Lebling et al, (2022) also reviewed many other problems of increasing to scale.

An additional problem with this type of DAC is that it does not have any immediate advantages such as improving crop yields, cutting down on N₂O emissions or combating ocean acidification and deoxygenation.

The following authors have proposed cheaper methods of using DACS.

Chen et al (2023) described a Direct Air Capture technique utilizing a Lewis acid-base hybrid sorbent with polyamine-Cu(II) complex enabling over 5.0 mol of CO₂ capture/kg sorbent, nearly two to three times greater capacity than most of the DAC sorbents reported to date. The hybrid sorbent is also amenable to thermal desorption at less than 90°C significantly reducing the energy cost of re-capturing the CO₂. In addition, seawater was validated as a viable regenerant, and the desorbed CO₂ is simultaneously sequestered as innocuous, chemically stable alkalinity (NaHCO₃). This technique allows using oceans as decarbonizing sinks and helps to combat ocean acidification. A **disadvantage** is that it requires stoichiometric amounts of OH^- , i.e., nearly 1 metric ton of NaOH, for 1 metric ton of CO₂ capture and sequestration.

Kar, S. et al (2023) described an integrated capture and solar-driven utilization of CO_2 from air. At the anode it utilized a plastic-derived ethylene glycol which was oxidized into glycolic acid over a Cu^{26} Pd⁷⁴ alloy catalyst. Thus, it utilized discarded plastic waste as an electron donor, and sunlight as the sole energy input, providing the potential for a lower cost method of CO_2 capture. **Zhu et al (2023)** described continuous CO_2 capture using an electrochemical reactor that uses less energy.

CO₂ to Solid Carbon Researchers at the Royal Melbourne Institute of Technology (RMIT) reported the development of a liquid metal catalyst that quickly converts CO₂ to solid carbon which can be stored indefinitely or turned into useful materials. (Esrafilzadeh et al, 2022). They used eutectic Ga In Sn alloy (galinstan) as a base liquid metal (LM) for producing LM mixtures that were used during this study. Eutectic refers to a mixture of substances that melts and solidifies at single temperature that is lower than the melting points of the individual components. Further research into this NET is needed to evaluate whether it is inexpensive and scalable.

CCS, CCUS, DCCS and DAC all have the disadvantage that they do not address two other serious problems with climate change and greenhouse gases - ocean acidification and atmospheric N₂O. The alternatives termed *ex situ* sequestration do not have these problems.

1. CCSM (Carbon Capture and Storage by Mineralization) Here CO_2 is removed from flu gas and other outputs of power plants and sequestered using ground up mafic and ultramafic rocks. This has the advantage that storage is safe and permanent, but the disadvantage that it only mitigates the CO_2 produced by power plants and does not remove CO_2 from the atmosphere.

2. Enhanced Weathering (EW) using Croplands, Non-croplands, and Oceans (OAE). These avoid the problems of burying gigatons of CO_2 gas and address ocean acidification.

The Equation that Once Saved Planet Earth – with Our Help Can Do It Again.

The atmosphere of Venus is 96.5% carbon dioxide resulting in a deadly temperature of 872 °F. By comparison, the atmosphere of the earth contains 0.04% CO₂ or 424 ppm and a temperature compatible with life. Schuiling (2013) pointed out that the difference between the two planets was the presence of **water on earth** which allows the CO₂ to be permanently mineralized based on the following equation, where the left-hand compound is **olivine**, an **ultramafic rock**.

$$\begin{split} (Mg,Fe)_2SiO_{4(s)} + 4H_2O_{(l)} + 4CO_{2(g)} &\leftrightarrow 2(Mg^{2+},Fe^{2+})_{(aq)} \\ &+ 4HCO_3^{-}(aq) \,+\, H_4SiO_{4(aq)} \end{split}$$

This reaction, sequestering CO₂, could only occur in the presence of water. The complete fate of the different parts of this equation are shown below.

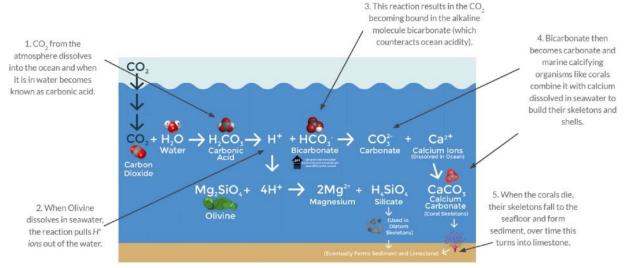
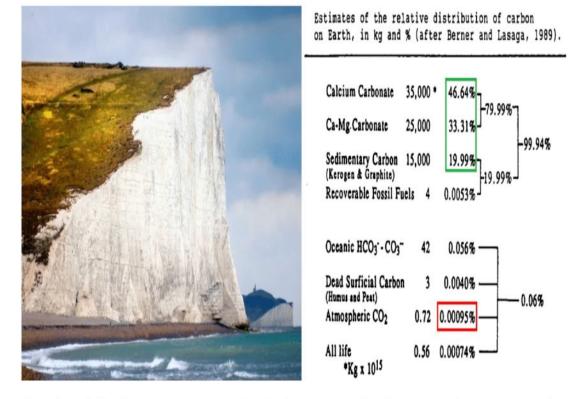


Figure from Project Vesta

 CO_2 from the atmosphere dissolves in water producing carbonic acid, H_2CO_3 which produces acidic H⁺ and HCO₃⁻. Ultramafic minerals such as olivine, Mg₂SiO₄ combine with the H⁺ to produce silicates H₄SiO₄ which are taken up by diatoms which die and fall to the ocean floor. The carbonic acid also produces carbonates CO_3^{2+} which combine with calcium Ca²⁺ to produce calcium carbonate CaCO₃ which is used by corals and shells of other marine organisms. Combined, these reactions permanently store in mineral form 99.94% of all the CO₂ ever produced on earth and make the earth a livable planet.

What do we mean when we say, "And with help can do it again?" The above reaction in nature took thousands of years. However, if the ultramafic rocks are ground to a fine power (the finer the better) and spread on croplands, non-croplands and the ocean, the rate of the reaction of dissolution can be dramatically accelerated. Much of the research cited below was devoted to identifying methods of accelerating this reaction.



The White Cliffs of Dover are an example of where 99.9% of carbon on Earth is sequestered.

This mineral storage is massively greater than that of all the trees and plants on earth.

Bertram and Merk (2020) suggested that the closer a CO₂ sequestration NET replicated natural processes the greater the public acceptance. EW and the various OAEs both mimic natural processes. For example, the alkalinity of the ocean increases naturally because of rock weathering in which >1.5 mol of carbon are removed from the atmosphere for every mole of magnesium or calcium dissolved from silicate minerals and 0.5 mol for carbonate minerals (e.g., calcite and dolomite). These processes are responsible for naturally sequestering 0.5 billion tons of CO₂ per year (Renforth and Henderson, 2017).

What the ideal CO₂ removal technique should accomplish.

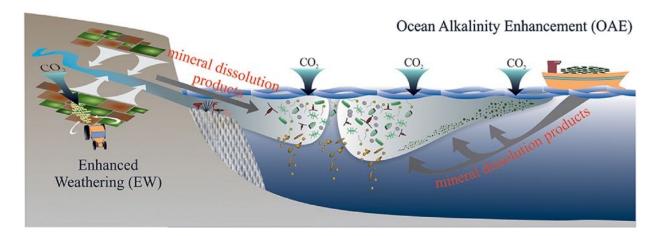
The following are the characteristics of an ideal method of removing CO₂ from the atmosphere.

• Provide for a permanent and safe long-term storage of gigatons of CO₂ for thousands or millions of years.

- Directly remove CO₂ from the atmosphere or ocean.
- Decrease ocean acidification.
- Decrease in ocean warming,
- Decrease in ocean deoxygenation,
- Decrease marine production of N₂O.
- Decrease the soil production of N₂O.
- Do not compete with regular croplands, but actually improve existing croplands.
- Largely avoid the restrictions of regulatory groups as compared to ocean iron fertilization and SRM (solar radiation management).

Enhanced Weathering utilizing croplands and non-croplands and OAE/eOAE/heOAE utilizing the oceans meet all these requirements.

Acceleration of weathering (mineralization) without underground storage can be realized by pulverizing and distributing gigatons of mafic and ultramafic Mg, Ca and Fe oxides onto land (termed "Enhanced Weathering (EW)") or sea (termed "Ocean Alkalinity Enhancement (OAE)." The following diagram illustrates these two approaches (Bach et al, 2019).



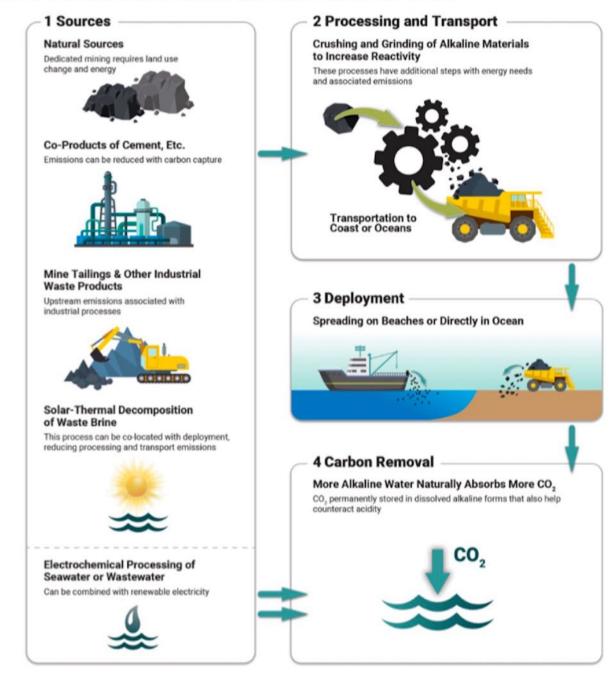
During EW, mineral dissolution products enter the ocean mostly via rivers so that perturbations first occur in estuarine and coastal regions. In the case of OAE, ships could transport the minerals to coastal regions or further offshore.

Not only do we believe that EW, OAE, eOAE and heOAE are the best NETs, we believe there needs to be an international effort in which most nations participate (see below)

Ocean Alkalinity Enhancement (OAE)

The following diagram illustrates the concept of OAE (EFI 2000b Uncharted Waters.)

Ocean Alkalinity Enhancement Approaches and RD&D Needs



Background Information

Before progressing further, we first present some Background Information on critical concepts. See **A through J.** The following articles are extensive reviews of ocean acidification (Riebesell et al, 2011), ocean alkalinity enhancement (Oschlies et al, 2023), and the Chemistry of CO₂ in Seawater (Dickson 2016), Dickson, et al (Eds.) (2007). Orr et al (2015) reviewed the 10 computer programs that compute ocean chemistry.

A. Alkalinity

It is important to differentiate between alkaline and alkalinity. Alkaline refers to a pH of greater than neutral as determined with a pH meter, while alkalinity or total alkalinity (TA) is more complex.

Since the concept of alkalinity is central to many issues relevant to EW and the OAEs, we will explain it in some detail. The following is from the paper by Bach et al (2019). An extensive review of alkalinity has recently been provided by Middelburg, et al., (2022). They begin their discussion using the **very technical definition** of alkalinity by Dickinson, (1981, 1992) of:

"The total alkalinity of a natural water is thus defined as the number of moles of hydrogen ion equivalent to the excess of proton acceptors (bases formed from weak acids with a dissociation constant $K \le 10$ - 4.5 and zero ionic strength) over proton donors (acids with K > 10-4.5) in one kilogram of sample."

More simply, **TA is defined as the excess of proton (H**⁺) **acceptors over proton donors** with respect to a certain zero level of protons (Dickson, 1981; Zeebe and Wolf-Gladrow, 2001; Wolf-Gladrow et al., 2007). In terms of chemical concentrations this reads in equation form as follows:

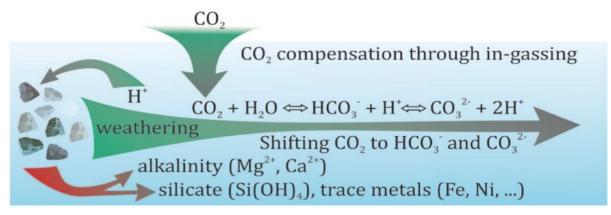
(1) $\mathbf{TA} = [\mathbf{HCO_3}^-] + 2 [\mathbf{CO_3}^2^-] + [\mathbf{B(OH})_4^-] + [\mathbf{OH}^-] + [\mathbf{HPO_4}^{2-}] + 2[\mathbf{PO_4}^{3-}] + [\mathbf{H_3SiO_4}^-] + [\mathbf{NH_3}] + [\mathbf{HS}^-] - [\mathbf{H}^+] - [\mathbf{HSO_4}^-] - [\mathbf{HF}] - [\mathbf{H_3PO_4}] + [\mathbf{H}^+] + \mathbf{is removed by OAE} -> \mathbf{increased TA}$

The dissolution of CO_2 in seawater and the subsequent reaction with H_2O have no effect on TA because the formation of proton donors and acceptors is balanced.

(2) $\operatorname{CO}_2 + \operatorname{H}_2\operatorname{O} \leftrightarrow \operatorname{H}_2\operatorname{CO}_3 \leftrightarrow \operatorname{HCO}_3^- + \operatorname{H}^+ \leftrightarrow \operatorname{CO}_3^{2-} + 2\operatorname{H}^+$

A shift of the carbonate chemistry equilibrium (Equation 2) toward HCO_3^- and CO_3^{2-} would coincide with decreasing CO_2 concentration so that additional CO_2 from the atmosphere could be absorbed and stored permanently. Such a shift toward HCO_3^- and CO_3^{2-} can be induced through the dissolution of minerals like **olivine** (Mg₂SiO₄) or **quicklime** (CaO). H⁺ is consumed during the dissolution of these minerals and replaced by conservative ions with positive charges (in our cases Mg²⁺ or Ca²⁺) (Pokrovsky and Schott, 2000; Wolf-Gladrow et al., 2007; Oelkers et al., 2018):

Olivine : $Mg_2SiO_4 + 4H^+ = 2Mg^{2+} + H_4SiO_4$ Quicklime : $CaO + 2H^+ = Ca^{2+} + H_2O$ The positive charges from Mg^{2+} and Ca^{2+} must be balanced by negative ones due to the constraint of electroneutrality (Wolf-Gladrow et al., 2007). The law of **electroneutrality** states that in any single ionic solution a sum of negative electrical charges attracts an equal sum of positive electrical charges. This ultimately forces a shift from CO_2 to HCO_3^- and CO_3^{2-} (figure below) and is measurable as an **increase in TA which is called "ocean alkalinity enhancement or modification."**



The above is a graphical summary of CDR through chemical weathering in aqueous media (e.g., soil pore water or seawater). When EW/OAE-relevant minerals (e.g., quicklime or olivine) dissolve they consume protons, H^+ , which shifts the carbonate chemistry equilibrium away from CO₂ to HCO₃⁻ and CO₃²⁻. Additional CO₂ can subsequently be absorbed by the aqueous media because the shift can cause CO₂ undersaturation relative to the surrounding atmosphere. For EW/OAE/eOAE/heOAE it is important that the dissolution occurs if the aqueous media is in contact with the atmosphere (e.g., in the surface mixed layer of the ocean) so that the under-saturated medium can be replenished with atmospheric CO₂.

The minerals appropriate for EW/OAE/eOAE comprise, for example, naturally occurring Mg-rich olivine-type silicates (Mg₂SiO₄) (Schuiling and Krijgsman, 2006). These may absorb 1 **Mt of CO₂ for every 1–2 Mt of olivine-rich rocks**. Dissolving one mole of olivine leads to an increase in total alkalinity by 4 moles and in silicic acid (H₄SiO₄) by one mole (Köhler et al., 2013). The energy expenses are due to mining, mineral grinding, and distribution (Moosdorf et al., 2014). For the definition of a mole see Appendix B.

B. Acidification

The cause, effects and treatment of ocean acidification were well covered by EFI (2019) *Clearing the Air*, and they are presented verbatim in Box 5-1.

Box 5-1 Ocean Acidification

The oceans currently absorb approximately a quarter of anthropogenic CO₂ emissions.¹⁷ As CO₂ dissolves in the ocean, it reacts with water to form bicarbonate ions (HCO₃-) and hydrogen ions (H₊). Most of the hydrogen reacts with existing carbonate ions (CO3)₂- to form additional bicarbonate, but some remains, acidifying seawater. This has led to a 30 percent increase in ocean acidity since the beginning of the industrial era, faster than any acidity change in the oceans over the last 20 million years.¹⁸

The reaction between hydrogen and carbonate ions depletes the amount of carbonate that is available for marine organisms such as shellfish and coral to form calcium carbonate (CaCO₃) for shells and skeletons (Figure 5-2).19,20 This problem is compounded by the fact that if acidification trends continue, seawater will become corrosive to these shells by the end of the century. Increased acidification also threatens corals, and bleaching events are becoming more common.21 Increased ocean acidification will also have major impacts on phytoplankton, the foundation of the entire marine food web.22

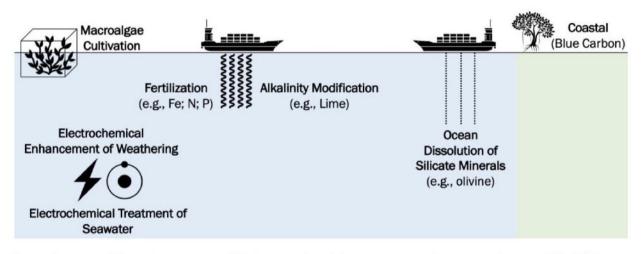
The relationship between CO₂ and ocean acidification may make it seem counterintuitive to actively store CO₂ in the oceans as a CDR technique. However, proposed CDR techniques such as ocean alkalinity modification (OAM) focus on storing carbon in the form of bicarbonate, chemically balanced by sources of alkalinity such as lime (CaO). These approaches would leave the pH of seawater unchanged or act to counter increasing acidification on a local basis. This can be an important co-benefit of these pathways in addition to their climate impact.



Some of the negative impacts of acidification are illustrated below.

Left: A healthy shell. Right: A shell affected by increased ocean acidity at pH and carbonate levels projected for the year 2100. Source: National Oceanic and Atmospheric Administration.

The following is an additional diagram of treatment options from EFI (2019) *Clearing the Air*.



Several opportunities exist to pursue CDR in coastal and deep oceans environments. Source: EFI, 2019. Compiled using data from the Joint Group of Experts on the Scientific Aspects of Marine Environmental Protection. Graphics from Noun Project.

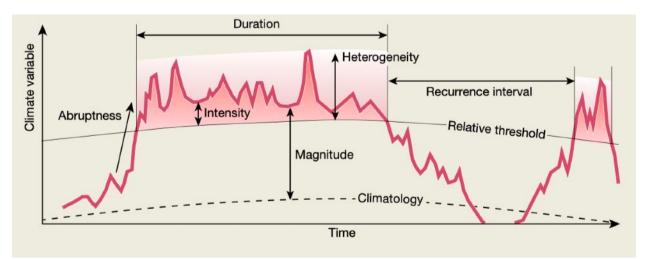
Some of these approaches are covered later.

C. Trio of acidification, warming and deoxygenation

In addition to acidification two other phenomena contribute to the negative effects that increased levels of atmospheric CO₂ have on the ocean – warming and low oxygen concentration. The deoxygenation is the result of the decreased solubility of oxygen in warmer oceans. This trio of acidification, warming and deoxygenation leads to extreme events with dramatic consequences. "For example, between 1982 and 2016, the number of days with marine heatwaves—defined here as days on which the sea-surface temperature (SST) exceeds its local 99th percentile—has doubled. Human-driven global warming caused the ocean surface to warm by around 0.4 °C, over this period. The trend towards more frequent marine heatwaves is projected to continue under global warming, with the ocean encountering 16 times more marine heatwave days compared with preindustrial conditions" (Gruber et al, 2021).

Ocean Blobs A particularly malignant form of localized ocean overheating was detected in October 2013. As described by the National Park Service, a strong and long-lasting high-pressure ridge in the Pacific Ocean created a mass of warmer-than-normal water by between 4- and 10-degrees F above average, that stretched over 1,000 miles between the North American and Asian continents and was up to 300 feet deep. It was the size of Texas and called the **Blob** after a Science fiction movie of the same name. It later split into three distinct masses between 2013 and 2018. This produced three patches, one in the Bering Sea, one off the California/Mexico coast, and one off the coast of Canada, Washington, and Oregon.

The many devastating effects of the **blob included killing phytoplankton which disrupted the entire Pacific food chain starving whales, salmon, herring, sardines, Alaskan cod, kelp, seals and others.** An elevation of nighttime temperatures even exacerbated forest fires (Goodell, 2023). The following figure shows the characteristics of these extreme warming, acidification, and deoxygenation ocean events.



Metrics associated with an extreme event includes the intensity, magnitude, duration, heterogeneity, abruptness, and recurrence (Gruber et al, 2021).

In their article *Let Oceans Breathe*, Goodkin and Pullen (2022) point out that while sea level rise and acidification have been the main focus of the effects of global warming on the oceans, **deoxygenation should have equal prominence**. They state that, "roughly **40 percent of the world's people depend on the ocean for their livelihoods**. If we do not save marine life from oxygen starvation, we starve ourselves." Penn & Deutsch, (2022) report that the current rate of ocean warming could bring the greatest extinction of sea life in **250** million years.

In a series of mesocosm studies Taucher et al (2022) reported that ocean acidification results in a decrease in the rate of dissolution of silica from diatoms. Silicon becomes progressively enriched in particles as they descend in the water column relative to the concentration of other elements. This results in a **decrease in surface concentrations of silica** (Hutchins, 2022). It was estimated that by 2200 this would cause a 13 to 26 percent decline in diatoms. An additional significant problem is the development in the ocean of warm blobs (Linden, 2022). These are increasing in frequency and have their own set of dire consequences.

D. DIC (Dissolved Inorganic Carbon)

The dissolved CO_2 can take several forms, including dissolved gaseous CO_2 , carbonic acid (H₂CO₃), bicarbonate ions (HCO₃⁻) and carbonate ions (CO₃²⁻). These are collectively known as **dissolved inorganic carbon (DIC)**, and the relative amount of each one is determined by pH (see Bjerrum Plot below). At normal seawater pH values, most DIC is in the form of bicarbonate ions **HCO₃⁻**.

Of the three forms dissolved CO_2 (non-ionic), is about 1% of the total, which can be exchanged with the atmosphere until the partial pressure in surface water and air are equal. Bicarbonate ion (HCO₃⁻) is about 91% and carbonate ion (CO₃²⁻) is about 8%. As atmospheric CO₂ increases, the dissolved CO₂ content of surface seawater increases at a similar rate, but most of the added CO₂ ends up as HCO₃⁻. Meanwhile, the CO₃²⁻ content decreases, since the net effect of adding CO_2 is a reaction with CO_3^{2-} to form HCO_3^{-} (Prentice, et al., 2001). Since this carbon is out of contact with the atmosphere, it is sequestered for the purposes of climate, and it can remain in this form for millennia. The net result of increasing ocean alkalinity is a decrease in atmospheric CO_2 .

The uptake capacity for CO₂ also varies significantly due to additional factors, most importantly seawater temperature, salinity, and alkalinity (the latter being a measurable quantity approximately equal to $[HCO_3^-] + 2 \times [CO_3^{-2}]$.

An important feature of DIC is that it is larger in the deep oceans than on the surface because of several "pumps," including upwelling/circulation (the "solubility pump"), phytoplankton photosynthesis (the "soft-tissue pump"), and the formation of hard shells (the "carbonate pump"). These pumps export carbon to the deep ocean and ocean sediments, separating it from the atmosphere for thousands of years or longer. They also keep the concentration of CO_2 in ocean surface waters lower than it otherwise would be, leading to continued removal of CO_2 from the atmosphere.

E. The Urey Equation

In 1952, Dr. Harold Urey (Urey,1952) of iridium/dinosaur killing meteor fame, provided the first successful attempt to explain the origin of the massive storage of carbon in the continental crust in the form of calcium carbonates in limestones and marble. "As carbon dioxide was formed it reacted with silicates to form limestones."

 $CaSiO_3 + CO_2 \leftrightarrow CaCO_3 + SiO_2$.

The silicates may have been in a variety of minerals, and the presence of atmospheric CO_2 was kept at a low level by this or similar reactions. The carbonation takes place when carbon dioxide (carbonic acid) in acid rain dissolves calcium silicate (wollastonite) sediments to give calcium, bicarbonate, and silica. The resulting calcium and bicarbonate ions flow in rivers to the oceans where either organic or inorganic precipitation produces the calcium carbonate. When water is included in the reaction (Blättler and Higgins, 2017) the formula becomes:

$$\begin{array}{rcl} \text{CaSiO}_3 + 2\text{CO}_2 &+ \text{H}_2\text{O} \rightarrow \text{Ca}^{2+} + 2\text{HCO}^{-3} + \text{SiO}_2 \\ \rightarrow \text{CaCO}_3 + & \text{SiO}_2 + & \text{CO}_2 &+ & \text{H}_2\text{O} \end{array}$$

One of the most famous massive accumulations of $CaCO_3$ is the White Cliffs of Dover. They date back over 136 million years, having been formed during the Cretaceous period in the Mesozoic era as the shells and skeletons of billions of tiny sea creatures fell to the bottom of the sea. They are composed of calcite (CaCO₃) from algae plankton called **coccolithophores**. When using silicates, such as olivine, the release of additional Si, Fe and Ni could benefit silicifiers and N₂-fixers such as cyanobacteria, diatoms, foraminifera, and coral) and increase ocean productivity. CO₂ consumed by silicate minerals (mafic rocks) is expected to be bound for millions of years, in part, due to carbonate precipitation in the oceans (Berner and Kothavala 2001).

This shows the immense duration of time that carbon is stably stored from natural weathering processes in which products of weathering are washed into the sea and taken up by various organisms which sink to the bottom and sequester carbon for eons. Enhanced weathering is simply the use of these methods to rapidly speed up this natural weathering process.

Massive Removal of Prehistoric Atmospheric CO₂ by Weathering

An indication of the immense ability of weathering to remove CO_2 from the atmosphere can be seen in geologic history. **Oceanic anoxic events (OAEs)** were times of abrupt carboncycle perturbations, driven by increases in atmospheric CO_2 largely the result of volcanic eruptions, as evidenced by the emplacement of **Large Igneous Provinces (LIPs)**. The cause of oceanic hypoxia following marked increases in atmospheric CO_2 is complex (Wignall, 2015), but **an increase in the metabolism of ocean organisms due to warming plays an important role**. When the global temperature raises, the rate of weathering increases. This functions as a **thermostat controlling the temperature of the atmosphere** (Brantley et al, 2023).

Between 55 and 200 million years ago there were 9 OAEs (Percival et al, 2016). Sequestration of CO_2 in organic-rich black shales and by reaction with silicate rocks exposed on continents would ultimately restore climatic equilibrium but at the expense of significant chemical change in the oceans and over time scales of tens to hundreds of thousands of years. This long duration reflects the amount of CO_2 spewed into the atmosphere amounting to **upwards of 2,000 ppm**. The fact that CO_2 levels were brought back to current levels indicates the **immense capacity of weathering to remove atmospheric CO_2** even though this took many thousands of years. Since the current CO_2 levels are 424 ppm, a decrease in atmospheric CO_2 by weathering would not take as long. In addition, the process can be markedly accelerated by the fine grinding and dispersal of olivine, serpentine and basalt.

F. CaCO₃: Aragonite, Calcite, Vaterite and Ω (omega)

Alkalinity required a special explanatory section because it is an important concept in understanding the use of OAEs. The same is true of various aspects of calcium carbonate, CaCO₃.

CaCO₃ occurs in three forms: aragonite, calcite and vaterite. The shells and skeletons of many marine organisms are made from either calcite or aragonite. Aragonite is of particular interest because it is produced by many tropical corals, cold-water corals, pteropods and some mollusks. It is more soluble than calcite. **Pteropods** are a group of **planktonic** gastropods that are widely regarded as biological indicators for assessing the impacts of ocean acidification.

Aragonite is formed by biological and physical processes, including precipitation from marine and freshwater environments. The crystal lattice of aragonite is an orthorhombic crystal system. It is more soluble than calcite.



Aragonite crystals Wikipedia

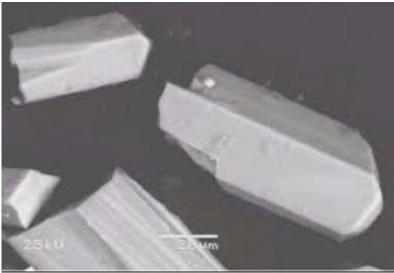
Aragonite is considered essential for the replication of reef conditions. It provides the materials necessary for much sea life and also keeps the pH of the water close to its natural level to prevent the dissolution of biogenic calcium carbonate.

Calcite the most stable polymorph of calcium carbonate. It has a trigonal crystal shape.



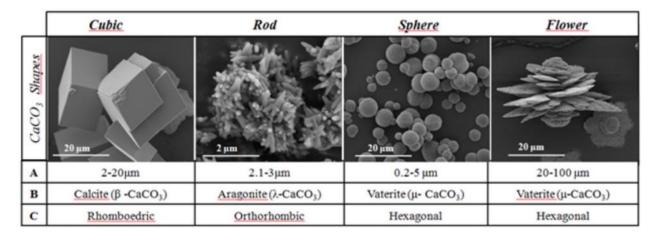
Calcite Wikipedia

Vaterite was named after the German mineralogist Heinrich Vater. It is also known as mu-calcium carbonate (μ -CaCO₃) and belongs to the hexagonal crystal system.



Vaterite Wikipedia

Recently, vaterite was found to have a huge potential for use as drug delivery carriers. The following figure shows the different crystalline forms of CaCO₃.



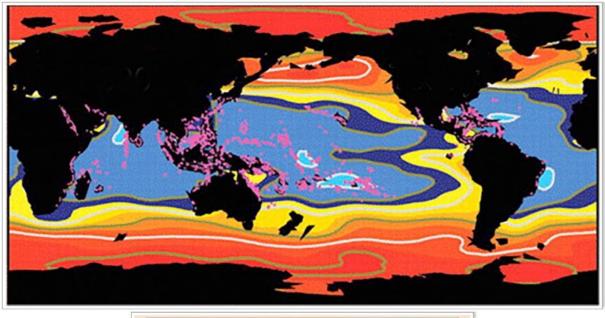
Crystalline forms of CaCO3 Medcraveonline.com

Omega The saturation state omega (Ω) describes the level of calcium carbonate **saturation in seawater**. The precipitation and dissolution of aragonite is seawater is shown by the following equation.

$$Ca^{2+} + CO_3{}^{2-} \ \leftrightarrow \ CaCO_3$$

$$\Omega = [Ca^{2+}] \times [CO_3^{2-}] / [CaCO_3]$$

If the saturation state for aragonite is less than 1 (Ω <1), conditions are corrosive (undersaturated) for aragonite-based shells and skeletons and the direction of the above equation is toward the left. If the saturation state is above 1 (Ω >1), waters are supersaturated with respect to calcium carbonate and conditions are favorable for shell formation with the direction of the above equation to the right. **Coral growth benefits from a saturation state of 3 (\Omega≥3).** The level of Ω calcite in the world's oceans are shown in the following figure.



0 1 2 3 4 5 Ω aragonite

Figure adapted from Hoegh-Guldberg et al., (2007) Coral reef locations are indicated by pink dots.

 Ω values are highest at low latitudes (straddling the equator). The majority of this region has Ω around 4, with a few pockets having $\Omega > 4.0$. The waters along the western coast of South America are the only exception, having Ω values around 3.0. The locations of the **pink dots representing coral reef locations** are consistently found in the regions with higher Ω values. Conditions for coral reef growth are:

- $\Omega > 4.0$: optimal
- $3.5 < \Omega < 4.0$: adequate
- $3.0 < \Omega < 3.5$: marginal
- Ω < 3.0: poor

A decrease in Ω calcite is occurring due to anthropogenic CO₂ emissions, contributing to the loss of coral reefs.

G. Serpentine and Serpentinization

Since the subject of serpentine and serpentinization is mentioned so often it is necessary to review what they are and mean. Serpentinization occurs when ultramafic rocks are exposed to circulating aqueous fluids at temperatures lower than 400°C, leading to the formation of serpentine phases. The combined formula for serpentines is:

(Mg,Fe,Ni,Al,Zn,Mn)2-3 (Si,Al,Fe)2O5(OH)4

Serpentine is a soft ductile mineral and its presence in the mantle wedge lubricates subduction of the oceanic plate. Production of serpentine in the oceanic crust produces hydrothermal fluids and releases gaseous methane and hydrogen, as observed along mid-ocean ridges. The pH of the hydrothermal fluids is generally low but under some conditions, notably at low temperature, may be high enough to be favorable to life. Serpentines are an order of magnitude more common than olivine.

The following formula shows the serpentinization for a single mineral outcome.

Serpentinization is essentially a hydration process.

 $3Mg^{2+} + 2SiO_2 + 5H_2O = Mg_3Si_2O_5(OH)_4 + 6H^+$

The following formulas show how serpentine, and olivine interact with CO₂.

$$Mg_2SiO_4 + 2CO_2 \implies 2MgCO_3 + SiO_2$$
(1)
[olivine] [magnesite] [silica]

$$Mg_{3}SiO_{3}(OH)_{4}+ 3CO_{2} \Rightarrow 3MgCO_{3}+2SiO_{2} + H_{2}O$$
(2)
[serpentine] [magnesite] [silica]

A disadvantage of serpentine is that **serpentine dissolution kinetics are significantly slower than those of olivine** (Blondes et al, 2019; Daval et al, 2013). **Increased heat and decreased pH increase dissolution rates**. Serpentine and serpentinites are much more mineralogically variable than olivine and peridotites. Serpentinization is thermodynamically favored in near surface environments and its products are stable on a geological time scale. Thus, **both olivine and serpentized olivine are effective in the sequestration of CO**₂.

H. Units of Weight

Before progressing further, it is informative to know the meaning of various metric terms.

Unit	Symbol	Order of Magnitude	Amount
peta	Р	10^{15}	quadtrillion
tera	Т	10^{12}	trillion
giga	G	10 ⁹	billion
mega	Μ	106	million
kilo	k	10 ³	thousand
milli	m	10-3	thousandth
micro	u	10-6	millionth
nano	n	10-9	billionth
picro	р	10-12	trillionth

In general use of the term picro refers to trillionth (10^{-12}) and the use of the term giga refers to billions (10^9) . The variable use of grams versus tons can also be confusing. One metric ton = one million 10^6 grams.

So, how much is a PgCO₂? As shown below, we often see a statement like "could perhaps extract 0.5-4 PgCO₂/yr, by 2100." It is not immediately obvious how much a PgCO₂ is. Did the P stand for petagram (10¹⁵)? The table above indicates that the symbol for a petagram is P. The definitive answer came from Canadell and Schulze (2013). They stated that:

"PgC per year (petagrams of carbon per year equals 10^{15} g equals a billion (giga) (10^{9}) metric tons)" Finally, an author made this term clear.

So how much is a ton of C? The atomic weight of carbon is 12 atomic mass units, while the weight of carbon dioxide is 44, because it includes two oxygen atoms that each weigh 16. So, to switch from one to the other, use the formula:

One ton of carbon (C) = 3.67 tons of carbon dioxide

I. RCPs (Representative Concentration Pathways)

Different numbered RCPs may be mentioned in the climate change literature. RCP refers to **Representative Concentration Pathways**. They represent different emissions, concentration and radiative forcing projections leading to a large range of global warming levels, from continued warming rising above 4 °C by the year 2100 to limiting warming well below 2 °C as called for in the Paris Agreement. The following table summarizes what the different numbers mean.

RCP	Forcing	Temperature	Emission Trend
1.9	1.9 W/m2	~1.5 °C	Very Strongly Declining Emissions
2.6	2.6 W/m2	~2.0 °C	Strongly Declining Emissions
4.5	4.5 W/m2	~2.4 °C	Slowly Declining Emissions
6.0	6.0 W/m2	~2.8 °C	Stabilising Emissions
8.5	8.5 W/m2	~4.3 °C	Rising Emissions

When combined with the **Socioeconomic Pathways (SSPs)** they provide a powerful framework to explore the space of future pathways in terms of different levels of mitigation stringency and different assumptions about socioeconomic development.

Note that currently, based on rising CO_2 levels in the atmosphere, we are still showing rising emissions with a disastrous potential temperature of greater than 2.8°C. We need to do something and do it quickly.

J. A Short Course in Mineralogy see Appendix A

End of Background Information.

US Geological Survey of Methods of Carbon Dioxide Storage

The emphasis in the present review is on the potential role of EW using cropland, noncropland, and oceans. The US Geological Survey published two important documents: USGS (2019) and Blondes et al, (2018). These documents reviewed techniques for CO_2 storage in the United States. Based on those and current literature there are five approaches.

1. CO₂ Storage: Injection of CO₂ **underneath rock formations** deep underground without mineralization. As noted above, these are potentially dangerous.

The next four types of CO₂ Mineralization are all versions of Enhanced Weathering.

In situ sequestration

2. CO₂ Mineralization: Injection of CO₂ into rock ultramafic formations deep underground *in situ* mineralization.

Ex situ storage

- 3. CO₂ Mineralization: Exposure of CO₂ to **pulverized rock at the surface**, using leftovers from mining, called **mine tailings.**
- 4. CO₂ Mineralization: Spreading **pulverized mafic rocks onto croplands and noncroplands**.
- 5. CO₂ Mineralization: Spreading pulverized mafic rocks onto the beaches or ocean.

Because of the potential danger of the escape of the CO_2 for #1, and the fact that several companies are already doing #2 (see below), our emphasis will be on #3, #4 and #5. But first we will discuss *in situ* sequestration.

In situ CO₂ sequestration

The *in-situ* sequestration of CO_2 involves injecting captured CO_2 **into mafic or ultramafic rocks underground where it is chemically bound to the rocks**. An extensive review of *in situ* sequestration is provided by Kelemen et al, (2019).

The first large scale effort to examine *in situ* CO_2 sequestration was in Iceland by Reykjavik Energy. The experiment called **Carbfix** took place at Iceland's Hellisheidi geothermal power plant (Matter et al, 2016). Starting in 2012, machines separated CO_2 and hydrogen sulfide gas—natural products of the geothermal sites—from the plant's exhaust and injected them through wells 400 to 800 meters back down into the basalt. Over eight months engineers injected about 250 tons of CO_2 . Monitoring at nearby wells showed that 95 percent of it was locked into carbonate minerals within two years. The project has operated ever since, storing roughly **10,000 tons of CO_2 per year**. In 2019 Carbfix was spun off as an independent company with the goal of **locking a billion tons of CO_2 into basalt by 2030**.

Since then, another team at Pacific Northwest National Laboratory in Richland, Wash., has also mineralized CO₂ in basaltic rocks—the **Wallula Basalt Pilot Demonstration**.

One of the places in the world where *in situ* sequestration is believed to have great promise is in **Oman on the Arabian Peninsula** and **New Caledonia**.



A recent report provides an update on this work (Fox, 2021). Peter Kelemen a geologist at the Lamont-Doherty Earth Observatory at Columbia University and his colleagues estimate that Oman's exposed mafic rocks are absorbing 100,000 metric tons of CO₂ every year by natural mineral carbonation. How far down does this carbonation occur? Drilling cores showed that it **does not go deeper than about 100 meters**. Since Oman's mantle rocks are on average about three kilometers thick, they realized there was a huge potential for carbonation if they could reach deeper down.

The plan by Kelemen, Matter and Lackner (Kelemen & Mater, 2008; Metter and Kelemen, 2009; Lackner and Matter, 2008; Paukert, et al, 2012; Kelemen, et al, 2019; Fox, 2021) was to utilize CO₂ **direct-air capture** machines, pressurize the CO₂ gas, mix it with water and send it down a borehole 1,000 to 3,000 meters deep into the surrounding mantle rocks. The water would seep through the rock's pores, eventually reaching a second hole as much as 1,000 meters away that would act as a return chimney where more gas could be concentrated in it again, for a return journey. Rock temperatures three kilometers down are about 100 degrees C. That heat would accelerate the reactions. Additional heat generated by the reactions themselves would help drive the circulation of warmed water back up the chimneys.

With sufficient increase in effort, they calculated that upwards of a **billion tons (gigaton)** of CO₂ could sequestered per cubic kilometer of rock per year. It is estimated there are 15,000 cubic km of relevant underground rock. There are similar outcrops in Alaska, Canada, California (Dickinson et al, 1996), New Zealand, New Caledonia, Japan, and other places. The worldwide storage capacity of these rocks, including Oman's, is estimated to be able to sequester 60 trillion to 600 trillion tons of CO₂ - roughly 25 to 250 times the amount that humans have added to the atmosphere since 1850. Compared to Oman, there are almost equally large massifs in New Caledonia and Papua New Guinea. The contiguous 48 US States contain relatively small bodies of peridotite that cumulatively have about the same mass as the Samail ophiolite (Fox 2021).

For this vision to materialize, it would be necessary to build an extensive, global infrastructure of machines that pull CO_2 from the atmosphere and inject it down wells drilled into mantle rock. A team of workers was scheduled to arrive in Wadi Lawayni Valley in Oman to conduct the world's first test of injecting and mineralizing CO_2 deep into mantle rock. If that experiment succeeded, it could be the first step toward transforming Oman, or even the greater Arabian Peninsula, into a major industrial center for managing the climate emergency.

Any down sides? Ballpark estimates suggest that trapping a billion tons of CO_2 in carbonate minerals could potentially increase the volume of the rock by up to a tenth of a cubic kilometer, equal to about 35 Empire State Buildings. This could conceivably cause the ground to rise by up to 30 centimeters a year. Kelemen thinks that to reckon with this issue, any gigaton-scale injection in Oman should occur near the shores of the Gulf of Oman, where engineers could drill diagonally into mantle rocks that sit below the shallow seafloor. Any bulging would probably occur on the seafloor, where it would likely be benign. And the site would obviously provide plentiful seawater to carry concentrated CO_2 , important because groundwater tends to be scarce in this desert nation.

What next? An Oman-based company named 44.01 (after the average molecular weight of CO₂) has received government approval to run the world's first pilot test of mineral carbonation in mantle rocks. They will start injecting freshwater containing CO₂ and an inert tracer chemical into a borehole. Researchers would monitor the levels of tracer, CO₂ and dissolved minerals in a second borehole around 100 meters away to determine how quickly water is traveling through the intervening rock and how much CO₂ is being stripped from it. If this experiment shows that CO₂ is mineralizing quickly the company plans to begin its first commercial injection operation in 2022. It would use freshwater or possibly treated wastewater to carry 10,000 tons of the gas a year down a single well, with hopes of eventually expanding to 100,000 tons a year. The company also plans further expansion.

Advantages of *in situ* CO₂ sequestration. There are some major advantages of *in situ* hybridization.

• It avoids the cost of mining, crushing and transportation of mafic and ultramafic rocks. As a result, it has been estimated that it is cheaper than *ex-situ* sequestration with ultramafic rocks (NAS, 2019).

• The chemical sequestration is reasonably rapid requiring about two years (Matter et al, 2016).

• It has the potential for sequestering massive amounts of CO₂.

• The CO₂ is safely sequestered for very long periods of time.

The **disadvantages** are:

• A variety of many machines are needed to extract CO_2 from the air and these processes are expensive, estimated at \$120 to \$220 or more per ton.

- Large amounts of energy are required.
- It will require a massive infrastructure.
- The problem of elevation of the land over the injection sites needs to be addressed.

• Oman is an absolute monarchy where the Sultan of Oman is both head of state and head of government. Companies located in Oman have priority over mineral rights. As long as the sequestration is done, who does it is not as relevant as getting it done.

DACS Direct Air Capture and Storage Re-visited Earlier I listed several problems with most plans for underground storage of megatons and gigatons of CO₂. **These problems may not apply to** *in situ* sequestration. While the sequestration of 100 trillion tons may be a bit of hyperbole, *in situ* sequestration needs to be explored since it could allow DACS to solve the problem of safe storage. Articles on the subject range all the way from claiming DACS is bogus (Schlosberg and Hart, 2021, Nogrady, 2021) to claiming that with considerable work, government, and private support, it can be the answer to global warming (Lebling K. et al, 2022a, b, Qui et al, 2022).

Fox (2021) suggested there were Oman like deposits in **California** and possibly other sites in the United States that could be used for safe *in situ* storage. We need to identify these sites and explore the possibility that gigaton levels of *in situ* storage can be done in the U.S.

Low Cost DACS? A key issue in DACS is cost. Some estimates suggest that that when done at the scale needed for gigaton storage it would consume a significant proportion of the national electricity supply. It would help if a much less energy intensive DAC system could be used. In this regard, Prajapati, et al. (2022) described a stackable artificial leaf system that **captures CO₂ with 100% efficiency and utilizes only a small amount of electricity**. This could be a promising less energy intensive approach to DAC. While there was a critical comment about using this to scale (Casado, 2022) and a response to the comment (Sarape, R. et al. (2022) it might potentially solve the energy problem for DACS.

Versus *ex situ*. Since the rocks do the extraction from the air, *ex situ* CO_2 sequestration, as with enhanced weathering using crop land, non-crop land or the oceans, avoids the cost of CO_2 extraction from the air, as well as the side effect of the ground rising. However, *ex situ* in turn has the cost of mining, grinding and transportation. When using the ocean, there are transportation costs, getting the rocks to the shipping ports, and the shipping itself. These are avoided with heOAE.

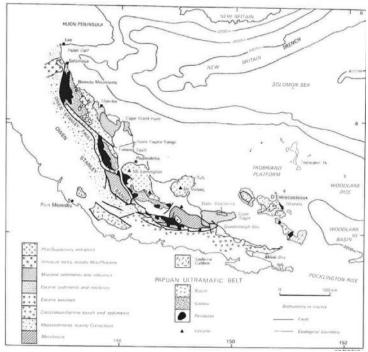
Ophiolites in New Guinea/New Caledonia - in situ or ex situ sequestration

As stated above, there are also **large massifs of ultra-mafic rocks in New Caledonia and Papua New Guinea comparable to those in Oman**. The following explores where these deposits are.

Ophiolites in New Guinea. The Papuan Ultramafic Belt marks a well-documented collision between continental crust and a subduction system (Smith 2013). To the southeast, there is an extensive sequence of basaltic rocks known as the Milne Terrain. Geochemical data indicate that these upper Cretaceous and Eocene rocks have MORB-type (Mid-Ocean Ridge

Basalt) affinities, and their most likely tectonic association is with the opening of the Coral Sea Basin. Milne Terrain rocks represent the lower plate in the obduction system along which the Papuan Ultramafic Belt was emplaced, and thus they are the structural equivalent of the continental crust which was separated from the Australian continental block by the opening of the Coral Sea.

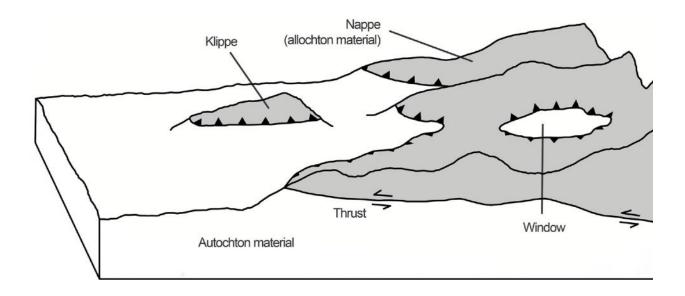
The following map shows the location of the **Papuan Ultramafic Belt** and Milne Terrain.



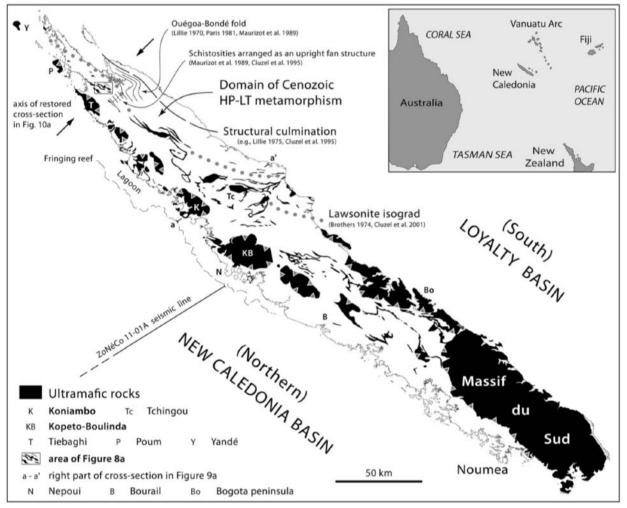
Papuan Ultramafic Belt (Davies and Jaques, 1984)

This map suggests that the northern coast of the Papuan Peninsula, near the town of Salamaus, where the ultramafic belt is closest to the ocean could a suitable site for mineable ultramafic rocks and research and for *in situ* sequestration.

Ophiolites in New Caledonia. The **Peridotite Nappe** of New Caledonia is one of the few ophiolites worldwide that escaped collisional orogeny after obduction. (Gautier, e al 2016). **Orogeny** refers to a process in which a section of the earth's crust is folded and deformed by lateral compression to form a mountain range. **Obduction** refers to the sideways and upwards movement of the edge of a crustal plate over the margin of an adjacent plate. Gautier et al (2016) described the deformation associated with **serpentinization** in two klippes of the nappe in northwestern. New Caledonia. A **klippe** (German for cliff or crag) is a geological feature of thrust fault terrains. A **klippe** is the remnant portion of a nappe after erosion has removed connecting portions of the nappe. A **nappe** is a large mass of rock thrust over other rocks. The following figure illustrates these terms.



A map of the location of ultramafic rock formations in New Caledonia is shown below. The Peridotite Nappe is mainly exposed in the "Massif du Sud," covering much of the southeastern third of the Grande Terre and in a series of klippes along the northwestern coast In the Massif du Sud, the thickness of the nappe is **at least 1.5 km but locally may reach 3.5 km**. The nappe is mostly composed of harzburgites. In the harzburgites, compositional layering is represented by 1 to 100 m thick layers of dunite.



Structural map of the Grande Terre, New Caledonia. The distribution of ultramafic rocks is slightly modified from Maurizot and Vendé-Leclerc (2009). Most of these rocks are originally part of the **Peridotite Nappe**.

The following is a relief map of the southern part of New Caledonia.



It is a mixture of moderate hills and flat places.

New Caledonia is an archipelago located in the Pacific Ocean to the south of the Equator. It is in the southwest Pacific Ocean, 1,300 km east of Australia. The **climate is tropical**, influenced by the trade winds, with a **hot and rainy season**, a cool and drier season, and two intermediate periods. The hot season is humid and rainy and runs from late December to late March. The temperatures in this season are high, around 30/32 °C (86/90 °F) during the day, but with peaks of 35 °C (95 °F). The humid heat is unpleasant, although the breezes make it more bearable; rain showers and thunderstorms are frequent. Rainfall is more abundant in inland elevations and on the north-eastern coast of the main island, where it exceeds 300 millimeters (12 inches) in the wettest month (March), while on the west coast, it ranges from 200 mm (8 in) in the north to 150 mm (6 in) in the south (see Nouméa).

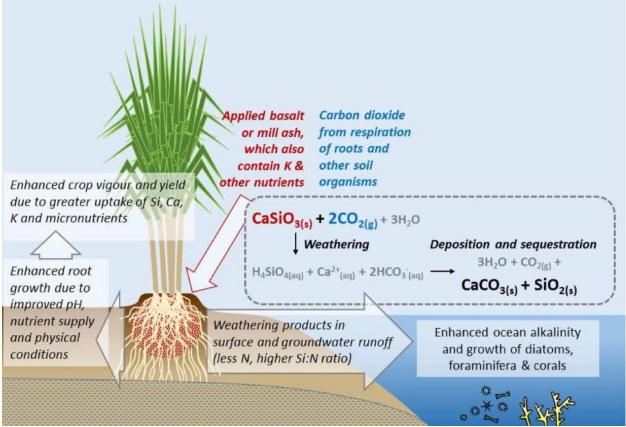
Multiple features make New Caledonia an almost ideal site for supply of ultramafic rocks for enhanced weathering both on land and in the ocean, as well as for *in situ* sequestration of CO₂. It is one of the only ophiolite areas in the world that has not been converted to mountains by orogeny and thus has plenty of surface ultramafic rock. Its tropical weather is consistent with it being a weathering hot spot (see below). Large amounts of ultramafic rock could be spread on flat land of the Grande Terre region. Kelemen and associates showed that natural carbonation of ultramafic rocks extended downward for 100 meters in Oman. This suggests that ground ultramafic rocks could be layered quite deeply, given that there is adequate rainfall.

In addition to these *ex-situ* uses of ophiolites **New Caledonia could also support** *in-situ* **use as in Oman.** Alternatively, it could be an excellent site for supplying ultramafic rock to be spread in the ocean to reverse the acidification at the nearby Great Barrier Reef and the rest of the ocean. In addition, it has an excellent port - Port Noumea.

The U.S. Geological Survey has a Regional Director of Pacific Islands, Dr. Jill Rolland, who could play a role utilizing this resource.

Enhanced Weathering using Cropland.

A form of accelerated weathering that also improves cropland is an NET consisting of spreading ground-up mafic and ultramafic rocks onto farmlands. This was proposed by Beerling et al (2018) and others (Hartman, et al 2008, 2012, 2013, Schuiling & Krijgsman 2006; Kohler et al, 2010; Taylor, et al, 2016, 2017; NAS 2018, 2019). EW using cropland is outlined in the following figure.



Concept of farming with crops and rocks by Beerling et al (2018) especially using olivine.

In soils, chemical breakdown of silicate rocks is accelerated during **aqueous reactions** with the elevated soil CO_2 environment, releasing base cations (Ca⁺⁺ and Mg⁺⁺) and delivering bicarbonate (HCO₃⁻) anions via runoff to surface waters and eventually the ocean. Enhanced weathering, therefore, also uses both the oceans and soil to store atmospheric CO₂ as these stable dissolved inorganic alkaline forms. Currently the oceans worldwide store around 38,000 Pg* C (38,000 gigatons) >45 times the mass of C in the current atmosphere.

* Pg = pentagrams = 10^{15} grams = 10^9 tons or one gigaton.

The residence time of dissolved inorganic carbon in the global ocean is around 100,000 to 1,000,000 years, making it essentially a permanent C-storage reservoir on human timescales. Thus, the residence time for enhanced weathering using croplands is also many, many years.

There are two potential types of minerals for this use: **carbonates** and **silicates**. Silicates are best because **carbonate weathering on acidic agricultural soils can lead to a net CO₂ flux to air** and carbonate minerals lack silica (Si) and other plant nutrient elements. Thus, the process of carbonate weathering on land delivers fewer benefits to climate, soils, and crops.

The silicate rocks are igneous, which means that they formed from cooled volcanic magma. Granite and basalt are the most common igneous rocks. Basaltic magma is what comes out when the earth's crust is cut through. As an eruption ends, the basalt "scab" heals the wound in the crust. Since it cools very quickly, the minerals have very little opportunity to grow and are very fine grained. Most of the ocean floor is basalt, and most of the continents are granite but there are **continental areas (Deccan traps) where the basalt is on the surface**. Carbonates have some distinct disadvantages (see below).

Ma = magnesium fic = ferric iron.

Mafic relates to a group of usually dark-colored minerals rich in magnesium or iron. Common mafic rocks include basalt, diabase, and gabbro.

Ultramafic rocks have lower silica content (less than 45%). They are dominated by **olivine, plagioclase,** and **pyroxene**. They are also known as **ultrabasic rocks**.

Peridotites have a high concentration of olivine and other silicate minerals.

Plagioclase is the name of a group of feldspar minerals that form a solid solution series ranging from pure albite, Na(AlSi₃O₈) to pure anorthite, Ca(Al₂Si₂O₈).

Pyroxene minerals are defined by their chemical composition and crystal structure. Their generalized chemical composition is described by the formula XYZ_2O_6 where X can be Ca, Na, Fe⁺⁺, Mg, Zn, Mn or Li. Y can be Mg, Fe⁺⁺⁺, Cr, Al, Co, Mn, Sc, Ti or Vn. Z can be Si, Al or a combination of both. A wide range of cation substitutions can occur in the X and Y positions.

Because of the improvement of soils, it has been said that "What really sets enhanced rock weathering on crops apart from other technologies is its enormous win-win potential." It could lock up as much carbon as a trillion trees. (Farber, D., 2022).

The following figure from Hills et al (2020) shows that many other rocks can be used. Some have CO_2 sequestering capabilities comparable to olivine.

TABLE 1 | Common minerals and their reactivity with carbon dioxide.

Mineral	Formula	Reaction pathway	Potential CO ₂ uptake (% w/w total weight)
Olivine (Fosterite)	Mg ₂ SiO ₄	$\mathrm{Mg_2SiO_4} + 2\mathrm{H_2CO_3} \rightarrow 2\mathrm{MgCO_3} + \mathrm{H_4SiO_4}$	63
Serpentine polytype	Mg ₃ Si ₂ O ₅ (OH) ₄	$Mg_3Si_2O_5(OH)_4 + 3H_2CO_3 \rightarrow 3MgCO_3 + 2H_4SiO_4 + H_2O$	48
Portlandite	Ca(OH) ₂	$Ca(OH)_2 + H_2CO_3 \rightarrow CaCO_3 + 2H_2O$	59
Brucite	Mg(OH) ₂	$Mg(OH)_2 + H_2CO_3 \rightarrow MgCO_3 + 2H_2O$	76
Larnite	Ca ₂ SiO ₄	$Ca_2SiO_4 + 2H_2CO_3 \rightarrow 2CaCO_3 + H_4SiO_4$	67
Anorthite	CaAl ₂ Si ₂ O ₈	$CaAl_2Si_2O_8 + H_2CO_3 + H_2O \rightarrow CaCO_3 + Al_2Si_2O_5(OH)_4$	16
Jennite	Ca9Si6O16(OH)2.6H2O	$Ca_{1.67}SiO_{1.57}(OH)_{4.2} + 1.67H_2CO_3 \rightarrow 1.67CaCO_3 + H_4SiO_4 + 1.77H_2O_3 + 1.67H_2O_3 $	47
Rankinite	Ca ₃ Si ₂ O ₇	$Ca_3Si_2O_7 + 3H_2CO_3 + H_2O \rightarrow 3CaCO_3 + 2H_4SiO_4$	38
Akermanite	Ca ₂ MgSi ₂ O ₇	$Ca_2MgSi_2O_7 + 3H_2CO_3 + H_2O \rightarrow 2CaCO_3 + MgCO_3 + 2H_4SiO_4$	48
Wollastonite	CaSiO ₃	$CaSIO_3 + H_2CO_3 + H_2O \rightarrow CaCO_3 + H_4SIO_4$	38
Tobermorite	Ca5Si6O16(OH)2.4H2O	$Ca_{0.83}SiO_{1.53}(OH)_{2.6} + 0.83H_2CO_3 \rightarrow 0.83CaCO_3 + H_4SiO_4 + 0.13H_2O_3 + 0.83CaCO_3 + 0.13H_2O_3 $	39
Pyroxene (Diopside)	CaMgSi ₂ O ₆	$CaMgSi_2O_6 + 2H_2CO_3 + 2H_2O \rightarrow CaCO_3 + MgCO_3 + 2H_4SiO_4$	41
Tremolite	Ca2Mg5Si8O22(OH)2	$Ca_2Mg_5Si_8O_{22}(OH)_2 + 7H_2CO_3 + 8H_2O \rightarrow 2CaCO_3 + 5MgCO_3 + 8H4SiO4$	38
Enstatite	MgSiO ₃	$MgSiO_3 + H_2CO_3 + H_2O \rightarrow MgCO_3 + H_4SiO_4$	44
Laumonite	CaAl ₂ Si ₄ O _{12.4} H ₂ O	$CaAl_2Si_4O_{12}.4H_2O + H_2CO_3 + H_2O \rightarrow CaCO_3 + Al_2Si_2O_5(OH)_4 + 2H_4SiO_4$	9

Where necessary, the reaction pathway has been normalized. Figures for % CO2 uptaken (w/w) assume the mineral reaction has been fully completed.

Of interest, brucite and larnite have even greater CO_2 sequestration than olivine. Because of this wide range of possibilities, a good geologist will be a critical member of a countries team.

Olivine

The most common ultramafic rocks are **olivine**, **dunite**, **periodite**, and **serpentine**. Dunite is rich in olivine.

Olivine is one of the most abundant minerals on Earth, making up over 50% of the upper mantle. When magma cools, olivine typically is the first mineral to crystalize. These volcanic rocks are typically located in the upper mantle, which is around 410 km (255 miles) below the surface of the Earth, making it all but inaccessible. The good news, however, is that due to tectonic forces there are areas of the upper mantle and seafloor that have been brought to the surface in a formation known as an **ophiolite**.

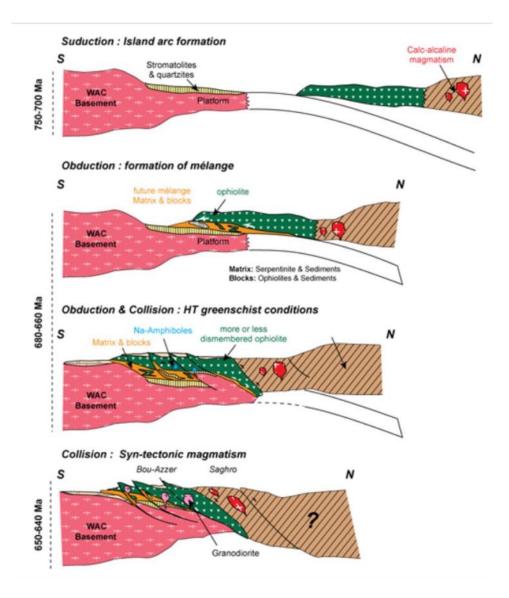
The following is a photo of my personal olivine-basalt that I purchased from a rock shop in Southern California.



The green crystalline olivine overlays a black, somewhat porous basalt.

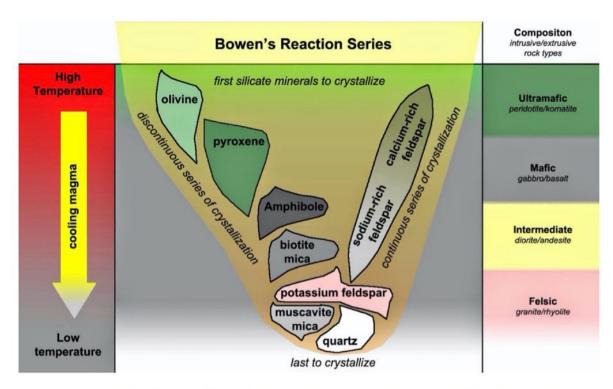
For those doing research on olivine reserves, if one searches for olivine, they will typically find only limited results. What to look for instead are the **ophiolites**. Ophiolites have an entire layer of olivine as the 90% pure form, dunite. And to further make it complicated to find olivine reserves, instead of seeing dunite listed, it is typically lumped into the category of **peridotites**. Ophiolite, olivine and periodite are typically found at the border between layers in the transition from the crust and the mantle, but this can vary depending on the specific formation (Project Vesta).

An example of different types of **ophiolite formation** are shown in the following figure of the Bou-Azzer Inlier of the northern margin of the Western African craton during the Pan-African epic. The **ophiolite is in green**.



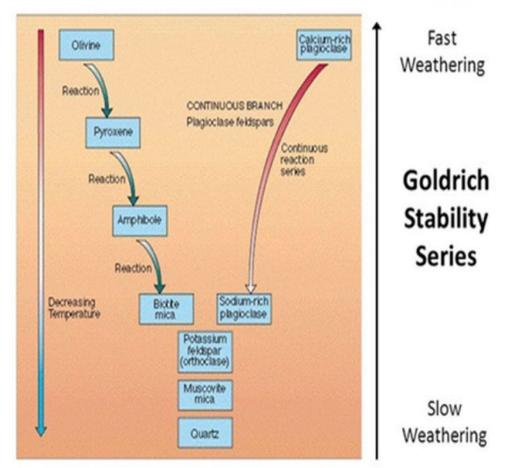
Model for the emplacement of the Bou-Azzer ophiolitic suite.

Olivine is one of the most rapidly weathering and thus CO₂ adsorbing, rocks in existence. Its chemical composition is $(Mg, Fe)_2SiO_4$. Sub-types are forsterite (Mg_2SiO_4) and fayalite (Fe_2SiO_4) .



Olivine is the first to form from when magma cools, and the fastest to breakdown from weathering forces.

As shown above in green at the top of the image, olivine - dunite is the endmember of a group known as **peridotites**, which is a generic term used for coarse-grained volcanic (ultramafic) rocks that form from the cooling and crystallization of molten magma. For weathering or mineral carbonation, any of the peridotites can be used. Olivine is the best due to it being the fastest weathering silicate (see Goldrich Stability Series - below).



The relevant equation for sequestration of forsterite olivine is:

$Mg_2SiO_4 + 4CO_2 + 4H_2O => 2Mg_2^{++} 4HCO_3^{-} + H_4SiO_4$

Thus, one mole of olivine can sequester 4 moles of CO₂ in the presence of water.

Schuiling (2013) had some interesting comments about this reaction.

"By this and similar weathering reactions throughout the history of the Earth, CO_2 was removed from the atmosphere. The resulting magnesium bicarbonate solutions are carried by rivers to the sea, where marine organisms (corals, shellfish, and plankton) convert them to carbonate rocks. This is the way by which 99.94% of all the CO_2 that has leaked out of the planet has been sustainably captured in rocks. **This has saved us from the fate of our sister planet Venus**, where weathering is impossible because Venus has no liquid water. All the CO_2 that was ever emitted by Venus has stayed in the atmosphere, leading to a CO_2 pressure of 85 bars and a surface temperature of $460^{\circ}C$."

Dissolved silicon is an important nutrient for diatoms, which produce a silicified cell wall, termed as frustule. Diatoms carry out a significant fraction of the net primary production taking place in the ocean (Ragueneau et al., 2000, 2010) and play a key role in the export of **particulate organic matter (POM)** to the deep sea. Because this export removes Si from the

surface ocean, Dissolved Silicon (DSi) determines diatom production in large areas of the world ocean (Dugdale and Wilkerson, 1998).

This stimulation of diatom growth in turn means that the supply of DSi has an important influence on the marine "biological carbon pump" (Ragueneau et al., 2000, 2006; Sarmiento et al., 2007), a set of processes in which carbon incorporated into POM through photosynthesis may be exported from the surface ocean to the deep ocean before its oxidation back to CO_2 . The carbon thus concentrated into the deep ocean is isolated from the atmosphere for the time it takes for the surface and deep ocean to mix (~1,000 years, on average).

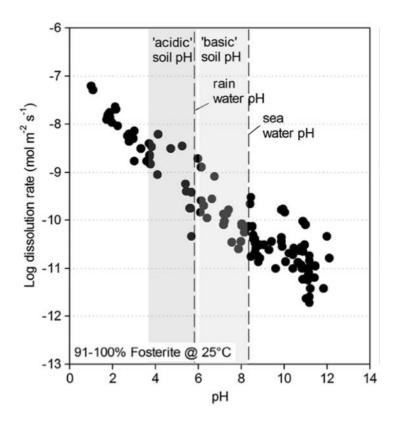
Effect of pH on Olivine Weathering

The following table shows the relative rate of weathering of olivine versus three other silicate minerals (basalt not included) at different pHs. Clearly olivine at pH 4 weathers very rapidly.

Mineral	pH 5.5	pH 4.0
Olivine	200-400	6000-8000
Pyroxene	14-25	20 - 200
Hornblende	26-30	100 - 200
Biotite	1.5 - 1.8	42-53

Rates of mineral dissolution (mg m²/day) obtained in the experiments of Franke & Teschner-Steinhardt (1994).

The three above non-olivine rocks can serve as approximate stand-ins for basalt. Like olivine, all three weather faster at lower pH and considerably more slowly than olivine. The following figure shows more detail about pH and olivine weathering.

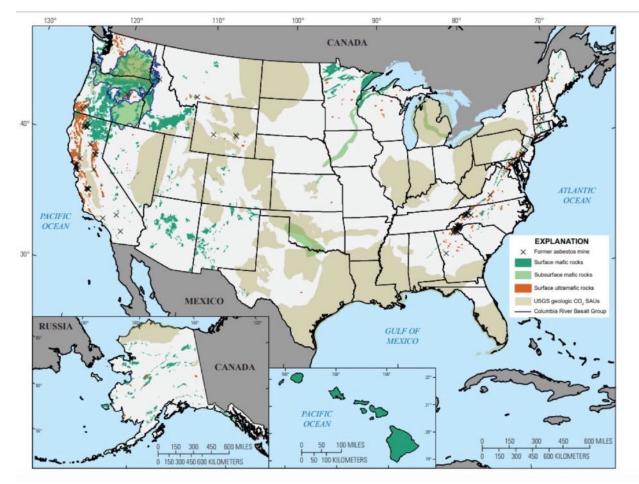


Dependence of olivine (Fosterite) dissolution on pH Figure from Hartman et al (2013)

The current average pH of ocean water is 8.1 while that of soil is 4 to 6. As can be seen, **olivine dissociates over ten times faster at the pH of soil than the pH of seawater**. Fosterite is the type of olivine that is rich in magnesium. It is the most abundant mineral in the mantle above a depth of about 400 km (250 mi).

Where are Mafic and Ultramafic Deposits in the U.S.?

The following USGS map shows the National map of mafic and ultramafic rocks in the United States compiled from multiple sources.



The surface mafic rocks are in dark green, the surface ultramafic rocks are in red. U.S. Geological Survey (USGS) geologic carbon dioxide (CO₂) **storage assessment units** (SAUs) (light brown) were defined in the USGS national assessment of geologic CO₂ storage resources (U.S. Geological Survey Geologic Carbon Dioxide Storage Resources Assessment Team, 2013) to estimate CO₂ storage potential in saline reservoirs within sedimentary basins.

It is clear that the vast majority of the surface mafic and ultramafic rock deposits are in the Western US – Washington, Oregon and California and Hawaii and Eastern US region. The sites in the Midwest (in light brown) are deep underground and presumably not economically viable for *ex situ* mineralization. All of Hawaii has surface deposits of mafic rocks. The following map is a clearer presentation of just the ultramafic (olivine) rocks in the U.S.

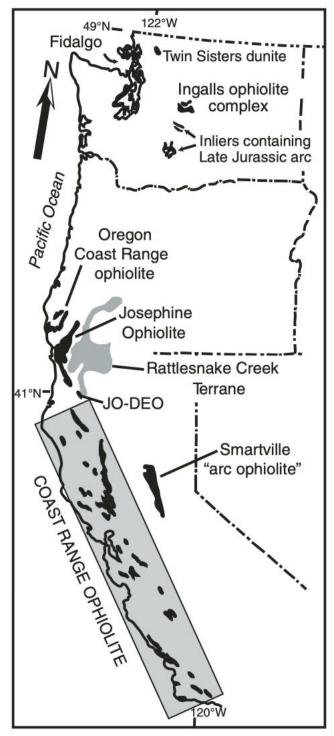


Ultramafic rock deposits in the U.S. The names of these sites are shown below.

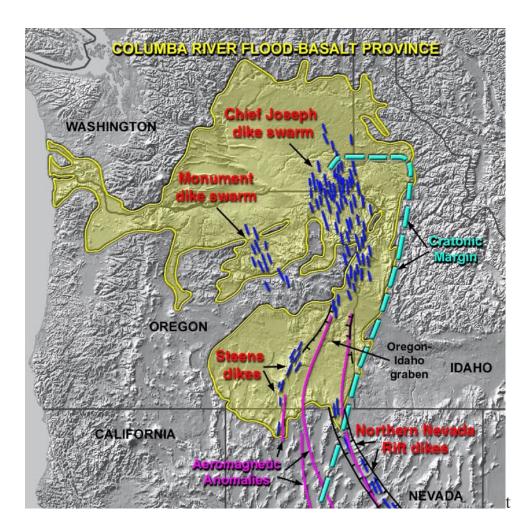


This shows the olivine deposits on the west coast and the east coast. Goff et al (2000) and Krevor, et al (2009) describe in detail the location of deposits of olivine deposits in Vermont, Baltimore, and Liberty Complexes (PA-MD-DC Region), Western North Carolina and Southwestern Puerto Rico.

The following diagram by MacDonald, et al (2008) shows additional details about the location of ultramafic rocks in the Western United States.



The map below shows in more detail the **basalt deposits** in the Columbia River Basin.

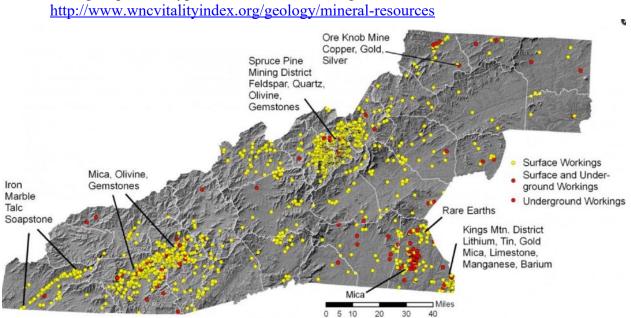


Columbia River Flood Basin

The following map shows the location of basalt deposits in the rest of the United States.



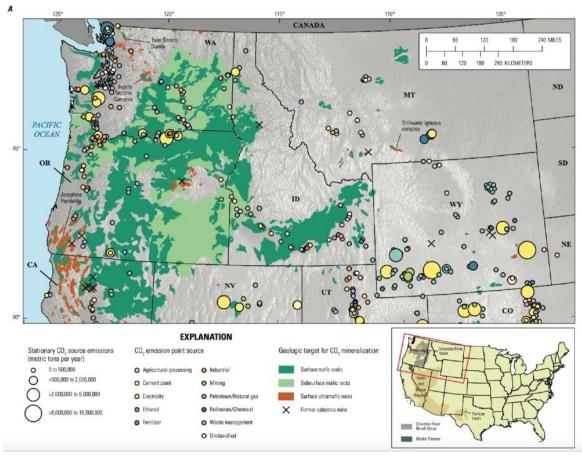
Credit: US Department of Energy/National Academies of Sciences, Engineering, and Medicine. Map of basalt formations (red) at and near the surface of the US that would be suitable for CO₂ sequestration.



The following map shows types and location of mining in North Carolina http://www.wncvitalityindex.org/geology/mineral-resources

The above map shows the details of the mining sites in North Carolina.

A more detailed map of the deposits of mafic and ultramafic rocks in the Western U.S. are shown by Blondes et al (2019).



Where to get Commercial Olivine or Basalt

The cost of commercially mined olivine is \$50 to \$110 per short ton (1.1 metric ton), depending on grade and size (Kramer, 2020).

Olivine produ		CONTRACTOR OF THE OWNER OF	ALL CALLER IN
(Thousand	metric	tons)	(e)
	1995	1999	
Norway	5,850	6,300	
Japan	900	900	
Spain	500	500	
United States	90	90	
Italy	50	50	
Others	40	65	
Total	7,430	7,945	

The U.S. production of olivine in 1999 was 90 metric tons/yr. The production in Norway was 6,300 metric tons/yr. It was mainly used in foundries for slag conditioning and foundry sand. The two U.S. companies that produce olivine are **Unimin Corp (Covia)** (North Carolina and Washington) and **Olivine Corp** (Washington) and the **Swen Larson Quarry**. The **reserves** in the **Smokey Mountains, North Carolina are about 200,000 million metric tons**, while the **reserves** in **Washington** are about 17 million metric tons. The total world production of olivine was approximately 8 million metric tons in 1999. North Carolina is the nation's major **olivine producer, with mines in Jackson, Mitchell, and Yancey Counties** (Seaman, 2006) (see maps above).

Unimin Corporation now called Covia, is a wholly owned subsidiary of global industrial minerals company SCR-Sibelco of Belgium. Unimin operates 44 mining and mineral processing facilities in the United States, Mexico, and Canada. In Mexico, the Company operates as Grupo Materias Primas de México and in Canada as Unimin Canada Ltd/Ltee. An additional large olivine site is Twin Peaks, OR (Lackner, 2002) and Twin Sisters, WA.

Norway is the main source of olivine in Europe, particularly in an area stretching from Åheim to Tafjord, and from Hornindal to Flemsøy in the Sunnmøre district. There is also olivine in Eid municipality. **About 50% of the world's olivine for industrial use is produced in Norway.** At Svarthammaren in Norddal olivine was mined from around 1920 to 1979, with a daily output up to 600 metric tons. At Robbervika in Norddal municipality an open pit mine has been in operation since 1984.

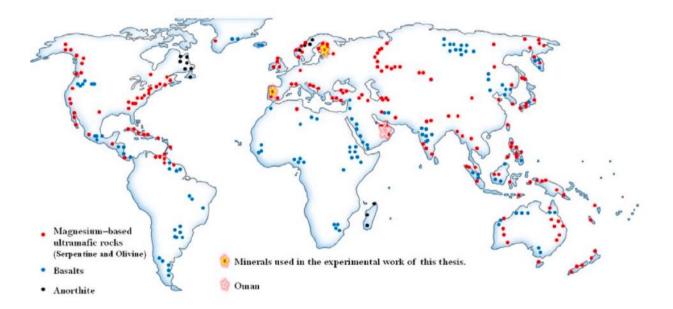
The table above (Kramer, 2020) showed that Norway is by far the greatest commercial producer of olivine at 6,300 thousand metric tons per year versus 90 thousand metric tons for the US.



The above shows the world's largest active olivine quarry, **Gusdal Pit**, in Norway. No chemicals are needed to extract the rock, nothing is underground, the process is not mining, it is surface extraction. This raises the possibility of purchasing olivine on site, ensuring it is finely ground, and immediately distributing it in the ocean.

Where are the Olivine Deposits Worldwide?

The following map shows the location of ultramafic rocks, olivine, and serpentines, throughout the world (Romanov, 2015)



A detailed list of worldwide location of ophiolites is present in **Appendix C. Worldwide Ultramafic Mining Sites and Companies** and shows many additional sites.

Weathering by Type of Land

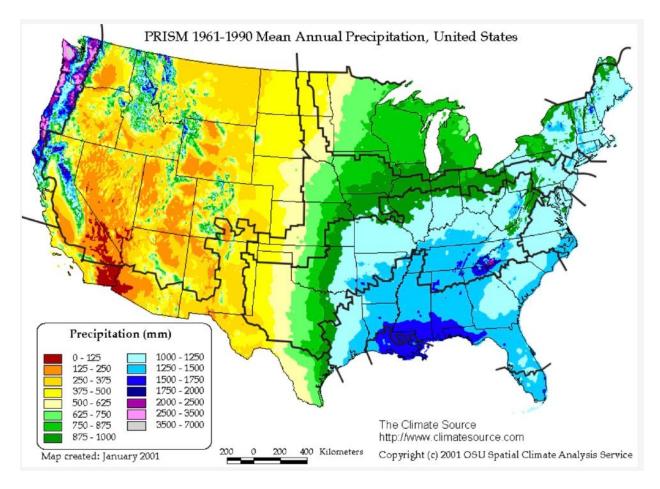
Weathering takes place faster in tropical and sub-tropical regions. But by how much? The following Table 3 is taken from Hartman and Kempe (2008) based on studies by Ludwig (1998).

	Area 10 ³ km ²	CO_2 consumed 10^6 t C a ⁻¹	CO_2 consumed t C km ⁻² a ⁻¹
Polar (without ice)	3,892	3.4	0.9
Tundra and Taiga	23,232	33.5	1.4
Temperate dry	9,635	4.4	0.5
Temperate wet	16,918	48.4	2.9
Tropical dry	21,790	15.1	0.7
Tropical wet	24,919	128.1	5.1
Desert	5,940	0.4	0.1

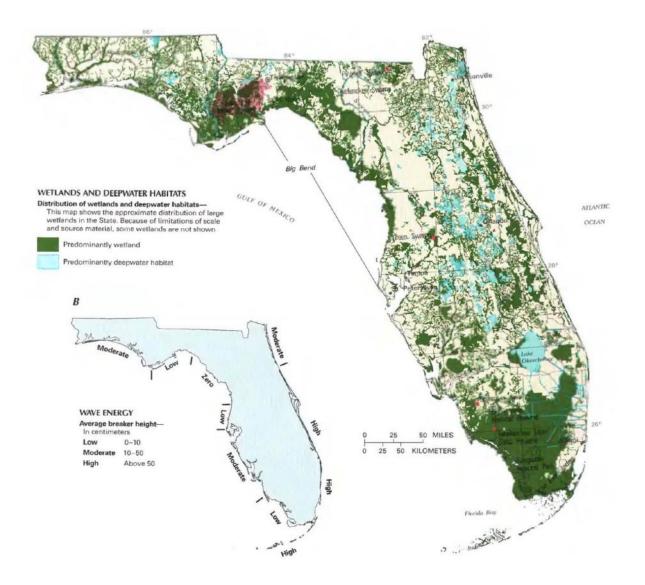
Table 3 Summary of considered mineral fertilization experiments.Average CO_2 -consumption per climate

 CO_2 uptake by rock weathering for different climates after Ludwig et al. (1998).

This shows that there is indeed a significant increase in sequestration of CO_2 by location and type of land. Sequestration is 29 times greater in tropical wetlands than in temperate try lands, and 2.4 times greater in the tropic wetlands than temperate wetlands. So where are the temperate wetlands in the US? The following map shows the annual precipitation in different regions of the US (The Climate Source, 2001).



Clearly the wet temperate regions in the US are in the southern states of Louisiana, Mississippi, Alabama, and Florida. The following is a more detailed map of the wetlands of Florida (Darst et al, 1991).



An additional factor that affects the rate of weathering is the presence of plants and forest vegetation (Hartmann, et al 2013).

The above data shows that there are many areas of temperate wetlands in the US. These are only 38% as efficient in weathering than tropical wetlands, but no "Hot spots" see below. **This should still be adequate for EWs projects in the US.**

Non-cropland

As discussed below, there are huge amounts of non-cropland in the U.S. Crushed olivine could be spread on this land and also planted with *Alyssum* plants to extract and sell nickel. This could make using non-croplands for EW economically more feasible. One question that needs study is, "How thick can the applied olivine on non-noncropland be and still sequester CO₂? If it could be up to 5 times the thickness of that applied to cropland, then it could be up to 5 times the effectiveness of EW on crops. This would considerably enhance the effectiveness of EW. If preferentially done in southern areas of high mean temperature and rainfall, as shown above, the multiplier could be even greater.

Basalt: Advantages and Disadvantages

The rate of chemical weathering of the basaltic Deccan Traps shows CO₂ consumption rates of $0.58-2.54 \times 10^6$ mol/km²/year (Dessert et al., 2001). Dissolved solid concentration in river waters, induced by basalt weathering on the Island of Réunion indicate CO₂ consumption rates of $1.3-3.4 \times 10^6$ mol/km²/year (Louvat and Allègre, 1997). Such values are equivalent to the consumption of up to **130 tons of CO₂ /km²/year**. With mine dumps of crushed ultramafic rocks, consumption of more than 4,000 tons CO₂/km²/year has been measured (Wilson et al., 2009).

In contrast to ultramafic olivine-rich rocks, major continental flood basalts have lower concentrations of Ni and/or Cr but significantly higher concentrations of phosphorus, suggesting their greater utility for croplands. Cultivation of crops on rich fertile soils that develop on flood basalts across continents is consistent with fewer environmental risks associated with this rock.

Basalt is widely recognized as producing productive soils **because it weathers rapidly releasing** elements essential for plant growth (Hinsinger, et al. 2001), including P, K, Ca, Mg and Fe. In terms of comparative weathering rates, olivine dissolution rates at oceanic pH~8 are within the range of those for basalt dissolution rates at pH 4 and above, expected in soils.

Significant potential exists for deployment at scale to remove atmospheric CO₂ with ground basalt. A maximum carbon capture potential of ~0.3t CO₂/t is suggested for basalt, assuming a sufficiently fine particle size for effective dissolution on decadal time scales (Renforth, 2012). The actual particle size will depend upon the mineralogy of the basalt, climate, and biological activity, and requires further investigation and verification, but initial calculations suggest particles of 10-30 μ m diameter. However, studies with olivine (see below) suggest rocks ground to 1 um size weather much faster.

On this basis, basalt applications of 10 to 50 t/ha/yr to 70×10^6 ha of the annual crops of corn or soy in the corn-belt of North America could sequester 0.2–1.1 PgCO₂, up to 13% of the global annual agricultural emissions (Kantola, et al 2017).

Theoretical estimates of CO₂ capture and sequestration schemes involving global croplands and silicate rocks are very uncertain. Provisional estimates (Smith, et al, 2016), suggest that amending two thirds of the most productive cropland soils (9×10^8 ha) with basalt dust at application rates of 10-30 t/ha/yr could perhaps extract 0.5-4 PgCO₂/yr by 2100 or 0.5 - 4 Gt CO₂/yr.

One of the consequences of climate change is an increase in the Nitrogen/ Phosphorus (N/P) ratio in soils and the ocean. The main **anthropogenic sources of reactive** N include the many kinds of nitrogen oxides from burning fossil fuels, the planting of N-fixing crops, and the use of N-rich fertilizers as well as their runoff into waterways. Although there are also human activities that have increased the amount of P in soils and waters—for example, from the application of P-rich fertilizers and detergents—the overall increase in the input of P is dwarfed by that of N. This increase in both N and P has led to eutrophication (excess of nutrients) of waters and soil.

The global N/P ratio of anthropogenic inputs has **increased from about 19:1 in molar basis in the 1980s to 30:1 in 2020.** The biological impacts of the increasing N/P imbalance have already been observed and reported in the trophic communities of several continental water bodies, in the structure and function of soil communities, and in the species composition of plants. P based fertilizers used to correct this imbalance, are increasingly unaffordable for farmers in the poorest countries.

As noted above, in contrast to ultramafic olivine-rich rocks, major continental flood basalts have significantly higher concentrations of phosphorus, (and less nickel) suggesting their greater utility for croplands. The use of basalts for EW would help to correct these aberrant N/P ratios.

Use of renewable energy A key issue affecting carbon capture efficiency is the energy cost associated with mining, grinding, and spreading the ground rock, which could reduce the net carbon drawdown by 10-30%, depending mainly on grain size. Relatively high energy costs for grinding, as influenced by rock mineralogy and crushing processes, calls for innovation in the industrial sector, such as grinding and milling technology **powered by renewable energy sources (solar, wind, microreactors or small nuclear molten salt reactors (MSRs)**, to significantly increase the net CO_2 benefit. The benefit will increase as future energy sources are decarbonized, the grinding process becomes more energy efficient, and by utilizing already ground waste silicate materials previously or currently produced by the mining industry, i.e., tailings. By driving down costs for grinding in this way, carbon sequestration costs would be correspondingly cheaper.

Nuclear Energy There are several companies and agencies that have been working for years on developing small, modular nuclear reactors. These are:

a) Terrestrial Energy Canada and USA. These are molten salt reactors that are super safe. See <u>www.TheComingsFoundaton.org</u> -> Molten Salt Reactors. When I called each company, the Canadian company expected to obtain approval in 2025 and the U.S. company in 2030. This time frame could be helpful for these projects.

b) NuScale Energy is making small nuclear reactors. It recently went bankrupt.

c) **The DoD Microreactor Initiative** In 2018 the Department of Defense issued a *Roadmap for the Deployment of Micro-Reactors for U.S. Department of Defense Domestic Installations.* The DoD manages 500 instillations, and this uses 21% of the total Federal energy consumption. The Micro-reactors were designed with island-mode operations, black-start capabilities, an ability to protect against severe natural phenomena as well as man-made physical and cyber security threats, and to operate for several years without the need to shut down for refueling. Small modular reactors, defined as less than 300 MWe, offer the ability to contribute to DoD missions The deployment of the first micro-reactor was expected to take between 5 to 10 years. Thus, it could be ready by 2028 or sooner, a time frame that makes it suitable to provide the power for grinding at the Twin Sisters facility (see below) and others.

Waste Materials – Tailings In regard to using waste materials, according to Renforth (2019) seven billion tons of alkaline materials are produced globally each year as a product or by-product of industrial activity. The aqueous dissolution of these materials creates high pH solutions that dissolve CO_2 to store carbon in the form of solid carbonate minerals or dissolved bicarbonate ions. He showed that these materials have a carbon dioxide storage potential of 2.9–8.5 billion tons per year by 2100, and may contribute a substantial proportion of the negative emissions required to limit global temperature change to $< 2^{\circ}C$.

Cost estimates for Basalt Current cost estimates are uncertain and vary widely, and better understanding the economics involved is a priority. The most detailed analysis for operational costs drawn-up for using a basic rock, such as basalt, gives values of US \$52-\$480 t/CO₂, with grinding and transport the dominant components (Renforth, 2012). This cost range falls below that estimated for bioenergy with carbon capture and storage (BECCS) of \$504-

\$1296 t/CO₂ (\$140-\$360 t/C) (Smith, et al, 2016). Deployment costs may be partially or completely offset by gains in crop productivity, and reduced requirements for lime, fertilizer, pesticide, and fungicide applications.

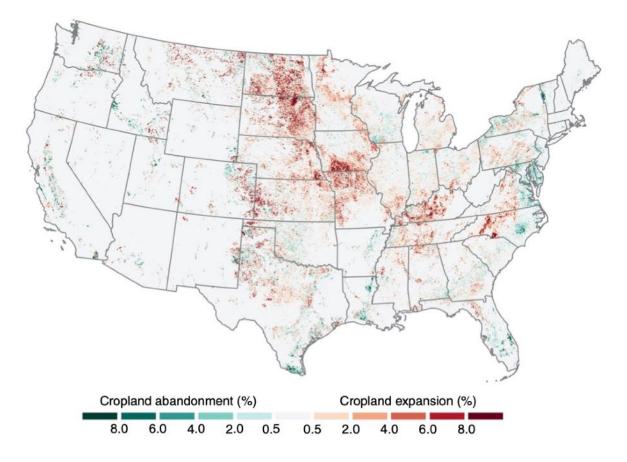
Given that farmers routinely apply granular fertilizers and lime, annual applications of ground basalt, an abundant, weatherable Ca- and Mg-rich rock, is feasible at large scale with existing farm equipment.

Silicon Enhancement of Soil Enhanced weathering strategies not only capture carbon but could also help restore soils and resupply impoverished reserves of trace elements important for human nutrition and crop production (Guntzer, et al 2012). The discovery of silicon transporters in several plants indicates the importance of this element. There are multiple ways in which silica helps plants in various types of environmental stress. Si fertilization makes soil phosphorus more available to plants. Seven out of the top ten crops ranked according to global production data (sugarcane, rice, wheat, barley, sugar beet, soybean, and tomatoes) are classified as Si accumulators (> 1%) and intensive cultivation and repeated removal of harvested products from the field is seriously depleting plant available Si in soils. In the US, for example, crop harvesting removes 19 million tons of Si annually (Tubana, et al (2016). Annual depletion of soil Si by continuous intensive farming, coupled with low solubility of soil Si, has led to calls for the development of viable Si-fertilization practices soon to increase plant available pools and maintain crop yields.

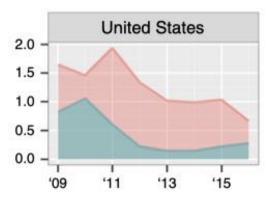
Dissolution of crushed silicates, or Si-containing mining and industrial wastes, releases Si, replenishing the plant available form. The fate and transformation of enhanced weathering derived Si in the soil-plant continuum, and its long-term biogeochemical cycling, warrant future research in the context of mitigating Si-related yield constraints on agricultural crop production.

An example of the use of crushed basalt in improving crop yields came from sugarcane trials with crushed basalt applications more than 20 t/ha in combination with standard NPK fertilizer treatments **increased yields by up to 30%** over five successive crops on the highly weathered soils of Mauritius compared with plots receiving fertilizer and no basalt addition.

Cropland Abandonment and Expansion in the U.S. Lark et al (2020) assessed annual land use change 2008–16 in the U.S. and its impacts on crop yields and wildlife habitat. They found that croplands have expanded at a rate of over one million acres per year, and that 69.5% of new cropland areas **produced yields below the national average**. They observed that some of this conversion infringed upon high-quality wildlife habitat especially relative to grassland milkweed critical for the Monarch butterfly. It also impacted on nesting opportunities for waterfowl in the Prairie Pothole Region of the Northern Great Plains. They thus demonstrated a pervasive pattern of encroachment into areas that are increasingly marginal for production, but highly significant for wildlife, and suggest that such tradeoffs may be further amplified by future cropland expansion.



Net cropland conversion 2008–16. Rates of net conversion calculated as gross cropland expansion minus gross cropland abandonment and displayed as a percentage of total land area within non-overlapping 3 km \times 3 km blocks. Net conversion was most concentrated in the eastern halves of North and South Dakota, southern Iowa, and western portions of Kansas, Kentucky, and North Carolina.



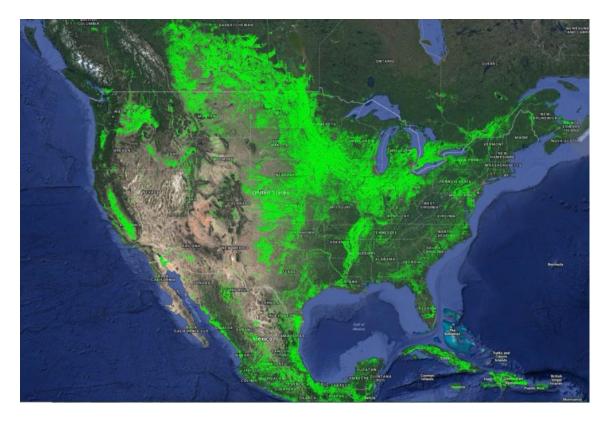
This figure summarizes the ratio of cropland abandonment (green) versus cropland expansion (red).

Carbon Emissions from Cropland Expansion In addition to the expanded cropland being less productive, an additional disadvantage is that such expansions release significant amount of the carbon stored in grassland (Spawn et al, 2019; EFI 2020a).

So, how is this relevant to the use in EW on cropland? A major finding was that the expanded croplands performed more poorly than regular cropland. If some of the newly converted areas, with the least disruption of wildlife, can be shown to have lower than average rates of crop production, they would be good candidates for EW. The expanded cropland involved a total of over 10 million acres. Such treatment might also reverse some of the negative effects on wildlife. Perhaps equally relevant would be the spreading of ground olivine, serpentine, or basalt on the abandoned cropland simply to sequester CO₂ independent of improving cropland.

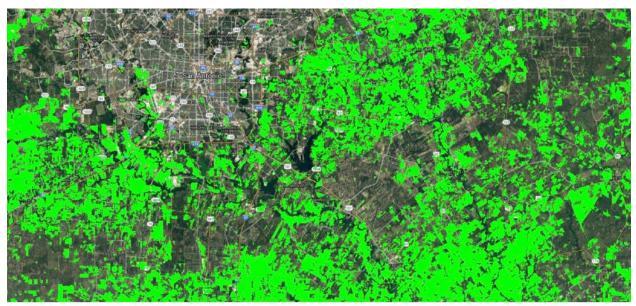
Non-cropland in the US The above showed the abandoned cropland in the US. The real issue is how much non-forest non-cropland is there in the US? The following map shows the cropland in the US. By default, also shows the non-cropland, which is extensive.

This map shows U.S. croplands in a nominal 30-m resolution derived primarily with Landsat imagery for the year 2015. The United States has 166 million hectares of net cropland area and is ranked second in the world after India, which has 180 million hectares of croplands. This is part of the GFSAD30 Project Landstat (USGS).



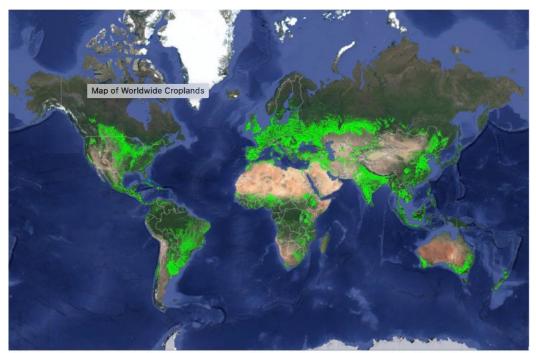
Cropland and non-cropland in the US

The following figure shows the power of the Landstat technology to investigate details of cropland and non-cropland.



This map shows croplands in Texas in a nominal 30-meter resolution. This is part of the GFSAD30 Project.

The resolution of Landstat allows the investigation at the level of individual farms. This will be invaluable in planning the sites and extent of ER on cropland.



The following figures cover the whole world.

This map shows cropland distribution across the world in a nominal 30-meter resolution. This is the baseline product of the GFSAD30 Project.

The combined above figures show that if EW were to involve both croplands and non-croplands, huge areas of land are potentially involved.

Calcium looping (CaL) (EFI, 2020c; McQueen et al, 2020)

Oxide looping is a Carbon Dioxide Removal (CDR) method that leverages the high reactivity of calcium (Ca) or magnesium (Mg) oxides and hydroxides to remove CO_2 from air. The starting materials are pure calcium or magnesium carbonate minerals. Heating them to temperatures of approximately 600°C to 900°C produces solid **calcium oxide or magnesium oxide and CO₂**. The CO₂ released during heating would then be captured and sequestered or used. The other byproducts, calcium, or magnesium oxide can be converted to calcium hydroxide (portlandite) or magnesium hydroxide (brucite), which react rapidly with atmospheric CO_2 to produce various solid carbonate minerals. The produced oxide/hydroxide sediment could be distributed in fields, tilled periodically to expose unreacted sediment, and recovered after a period of months to years to begin the process again.

If the total known global reserve of **magnesite** (MgCO₃) were to be mined and employed in this process, and if it were 100 percent efficient, **it could remove approximately 4 Gt CO₂ per year from the atmosphere**. Conversely, Ca looping, which is already used as a carbon capture technology for power generation, starts with pure limestone, a regionally widespread commodity of vast abundance. Limestone is quarried in vast quantities for cement and concrete production, used as a soil amendment in agriculture, and as a building stone. Thus, CaO might be preferable to MgO in many regions, despite the higher calcining temperature.

Calcium and magnesium oxide looping has not yet been demonstrated beyond laboratory and limited-scale outdoor experiments. Models suggest that 2,000 to 7,000 km² of land would be required per Gt of CDR per year, covered with oxide or hydroxide sediment about 5 cm deep. This amount of land is on the scale of the 100 to 200 largest mines in the world, but this technology has the potential to be a more efficient and long-lived CDR pathway than mineralization at industrial sites if the required land use can be justified.

CDR Method	Possible CDR Capacity (GtCO ₂ /yr.) and Land Use (km²/Gt/yr.)	Estimated Cost (per tCO ₂)	Possible Co-Benefits	Issues, Risks, Limitations, Uncertainties	Technology Readiness	
Carbonation of Mineral Wastes	2-9 Gt/yr. >2,000 km²/Gt/yr. using existing mines	Tailings management practices: \$10s CO ₂ injection: <\$50 Accelerated leaching: >\$50	Mitigating heavy metal/dust mobility; slope stabilization via cementation; potential integration with point-source capture	etal/dušt bility; slope abilization via mentation; tential egration with int-source etal/dušt Reactivity of minera wastes; carbon accounting frameworks		
Enhanced Rock weathering and Carbonation in Soils	<1-2 Gt/yr. (cropland only) >10,000 km²/Gt/yr.	\$8-\$100, depending on feedstock	Enhancing carbonate alkalinity in the oceans, delivery of essential trace nutrients to plants and soil microbes	Soil contamination; efficiency/rate of mineralization in soil environment; opening new mines to quarry fresh rock	Medium	
Calcium and/or Magnesium Oxide Looping	~4 Gt/yr. (global magnesite reserves) >400 Gt/yr. (including limestone)	\$50-\$150		Efficiency and timeframe; minimizing carbon from heating; identifying practical feedstock	Low to Medium	

Summary of CDR Methods ((EFI, 2020c)

Summary of Characteristics of Selected Mineralization CDR Methods

A company called **Heirloom Carbon** (1155 Indiana St, San Francisco, CA 94107) proposes to use this technique **for capturing gigatons of atmospheric CO₂**.

Note that Fakhraee et al (2022, 2023) (page 192 - 195) concluded that CaO and MgO were far superior to olivine for OAE sequestration of CO_2 and less stressful on the phytoplankton.

Ex-situ Sequestration

During WWII there was considerable interest in using ultramafic rocks as a source of magnesium and much research was devoted to enhancing this process. Later, the same techniques were used to enhance the carbonation or CO_2 uptake of these rocks especially as it relates to removing CO_2 from flue gas for purposes of combating the release of CO_2 by industrial processes.

The most studied mineral for *ex-situ* carbon mineralization was **olivine**. It is abundant, has a high reaction rate, and exhibits little passivation (coating). While the optimum temperature for carbon mineralization of olivine is ~185 °C. (O'Connor 2005) **it can also be used without this pretreatment**. However, these *ex-situ* approaches with their requirement for mining, grinding and transportation are more expensive than the projected cost of direct air capture of CO_2 and *in situ* storage, and more expensive than CO_2 storage in subsurface basalt domes. As a result, the cost of *ex situ* carbon mineralization could be several-fold higher than CO_2 injection and sequestration into subsurface reservoirs (NAS, 2019). **However, if the cost of grinding, the greatest cost, is covered by renewable energy, these costs would be considerably reduced**. A disadvantage of *in situ*, is that sites suitable for *in situ* sequestration are somewhat limited or undeveloped (see section on *in situ* sequestration). The numerous potential problems with DACS were covered previously (p 21-24).

The added conclusion that that the dissolution rate of ultramafic rocks in native soil is several folds slower than for laboratory studies (see below) would seem to count against this technique. However, there are several unique advantages of *ex situ* sequestration that make up for these disadvantages. These include the **improvement of croplands production and combating ocean acidification using eOAE technology**. In addition, because of the wide availability of olivine, basalt and serpentine deposits, *ex situ* sequestration and improvement of croplands can be done in many countries.

EW will also become a valid alternative to supply phosphorus or potassium to soils. Because of limited supply of current fertilizers, this alternative fertilizer for certain regions needs to be developed to enhance productivity. This is especially true for Africa.

Sandalow, D. et al (2021) This ninth ICEF roadmap explores a topic that has received too little attention: the potential for carbon mineralization to play an important role in helping fight climate change. There are two broad approaches to increasing the amount of CO_2 removed from the atmosphere via carbon mineralization: injecting CO_2 -rich fluids into rock formations deep underground (*in situ* mineralization) and exposing crushed rocks on the Earth's surface to atmospheric CO_2 (*ex situ* or surficial mineralization).

As a strategy for CO_2 removal and sequestration, carbon mineralization has many strengths. First, **mineralization resources are effectively unlimited** and located in dozens of countries around the world. Second, carbon mineralization offers one of the **most permanent** forms of CO_2 removal and sequestration available, binding CO_2 into solid rock. Third, the chemical reactions that mineralize CO₂ do not require energy inputs. Finally, **the costs of carbon** mineralization appear to be reasonable and could be reduced.

The authors estimate that, with strong and sustained policy support from governments around the world, carbon mineralization processes could remove 1 GtCO₂ from the atmosphere per year by 2035 and 10 GtCO₂ per year by 2050. More research is needed to test this hypothesis and define conditions under which carbon mineralization could achieve this potential.

The main challenges of EW are the lack of widely accepted methodologies for determining CO₂ removal rates and concerns about environmental risks from accumulation of metals, including **nickel and chromium. These, however, are manageable** (see p 215-228).

The following are some of their other findings.

• Carbon mineralization has the potential to permanently remove and sequester many gigatons of CO_2 from the atmosphere each year.

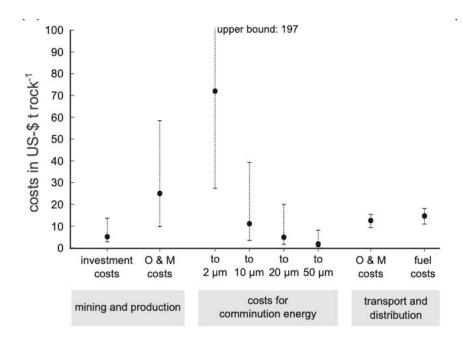
• As a strategy for carbon removal and sequestration, carbon mineralization has many strengths.

• Current scientific knowledge and technical experience are sufficient to support carbon mineralization projects at the pilot and demonstration scale today.

• Carbon mineralization receives little recognition or support in climate change policies around the world.

Strefler, J. et al (2018) state that they have provided the first comprehensive assessment of economic costs, energy requirements, technical parameterization, and global and regional carbon removal potential using Enhanced Weathering. The crucial parameters defining this potential are the grain size and weathering rates. They did not only assess dunite rock, predominantly bearing olivine but focused also on basaltic rock to minimize potential negative side effects. Their results showed that enhanced weathering is an option for carbon dioxide removal that could be competitive already at 60 US \$/t CO₂ removed for dunite, but only at 200 US \$/t CO₂ removed for basalt. The potential carbon removal on cropland areas could be as large as 95 Gt CO₂/yr for dunite and 4.9 Gt CO₂/yr for basalt. The best suited locations are warm and humid areas, particularly in India, Brazil, South-East Asia, and China, where almost 75% of the global potential can be realized.

The following figures illustrates how rapidly grinding costs increase with decrease in particle size. We proposed that these costs can **be negated using renewable energy**.



Summary of cost estimates. Filled circles show the selected best estimates and whiskers the lower/upper bound. O & M = operation and maintenance costs.

Rau G H et al (2007) Use of limestone. The use of accelerated weathering of limestone (AWL) utilizing the $CO_2 + H_2O + CaCO_3 \rightarrow Ca^{2++} + 2HCO_3^-$ reaction was explored as a CO_2 capture and sequestration method. The dissolved calcium bicarbonate produced is then released and diluted in the ocean where it would add minimally to the large, benign pool of these ions already present in seawater. Such a process is geochemically equivalent to continental and marine carbonate weathering which will otherwise naturally consume anthropogenic CO_2 .

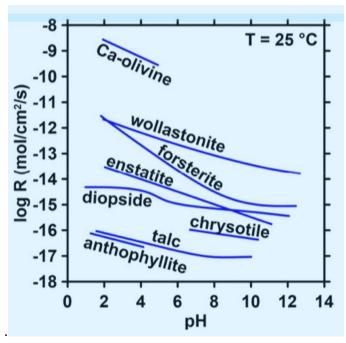
The authors showed that significant limestone resources are relatively close to most CO₂emitting power plants along the coastal US. Waste fines, representing more than 20% of current US crushed limestone production (4,109 tons/yr), could provide an inexpensive or free source of carbonate for AWL. With limestone transportation as the dominant cost variable, CO₂ mitigation costs of \$3-\$4/ton appeared to be possible in certain locations. Perhaps 10–20% of US point– source CO₂ emissions could be mitigated in this fashion. It is experimentally shown that CO₂ sequestration rates of 10⁶ to 10⁵ moles/sec/m² of limestone surface area are achievable, with reaction densities on the order of 10^2 tons CO²/m³/day, highly dependent on limestone particle size, solution turbulence and flow, and CO² concentration.

Based on the stoichiometry of reaction 1, it would take 2.3 tons of calcium carbonate and 0.3 tons of water to react with 1 ton of CO_2 to form 2.8 tons of HCO_3^- in solution.

US production of this mineral is presently 109 M tons/yr, about 76% of which is used in construction. Channeling the entire yearly US limestone production to AWL could consume roughly 18% of the annual CO₂ generated by electricity production in the US. This implies that a substantial increase in the US limestone mining rate or foreign importation would be required to accommodate the US demands of both extensive AWL and conventional limestone uses.

Modeling showed that AWL would also allow carbon storage in the ocean with significantly reduced impacts to seawater pH relative to direct CO_2 disposal into the atmosphere or sea. Storing waste CO_2 in the form of bicarbonate balanced by calcium ions rather than as dissolved CO_2 (i.e., carbonic acid; bicarbonate balanced by H+) substantially lessens the increase in acidity per ton of carbon added to the ocean while reducing harmful effects to marine biota of direct ocean CO_2 additions. The addition of AWL-derived alkalinity to the ocean may itself be beneficial for marine biota.

Schott, J. et al (2009) reviewed the dissolution rates of different rocks. The results are shown in the following figure.



The dissolution rate of Ca and Mg silicates at 25 °C as a function of pH (Schott et al, 2009)

Additional studies on dissolution rates are given below.

The subject of *ex situ* sequestration can be broken down into the following subjects:

- I. Olivine Dissolution: Laboratory Studies
- II. Olivine Dissolution: Field Studies on Cropland or Simulated Cropland
- **III.** Serpentine Dissolution: Laboratory Studies
- IV. Serpentine Dissolution: Field Studies on Cropland or Simulated Cropland
- V. Basalt Dissolution: Laboratory Studies
- VI. Basalt Dissolution: Field Studies on Cropland or Simulated Cropland
- VII. Wollastonite Dissolution: Field Studies on Cropland or Simulated Cropland
- **VIII.** Concurrent Grinding
- IX. Olivine: The Potential Role of Electrolysis
- X. Serpentine: The Potential Role of Electrolysis
- XI. Ho et al (2023) Using clay to adsorb and store CO₂

XII. The Koornneef et al (2009) Study

XIII. Enhanced Weathering Conference (2022)

I. Olivine Dissolution: Laboratory Studies

Olivine is a nesosilicate, or orthosilcate, mineral with the general formula $(Mg,Fe)_2SiO_4$. The olivine group consists of **forsterite** (Mg_2SiO_4) and **fayalite** (Fe_2SiO_4) . Olivine dissolves **quickly in comparison to other silicate minerals**. At Earth surface temperatures, olivine dissolution usually occurs stoichiometrically. The general reaction for olivine, specifically **forsterite**, dissolution is:

 $Mg_2SiO_4 + 4H_2CO_3 = 2Mg^{2+} + H_4SiO_4 + 4HCO_3^{-}$

During WWII there was considerable interest in using ultramafic rocks as **a source of magnesium** and much research was devoted to enhancing this process. Later, the same techniques were used to enhance the carbonation or CO_2 uptake of these rocks especially as it relates to removing CO_2 from flue gas.

The following Table 1 from Azadi et al (2019) illustrates the many techniques used to increase the dissolution rate ultramafic rocks, especially serpentine. The references cited can be found in the Azadi article.

Strategy Refe		Method	Benefit		
Mechanical pretreatment of serpentine rock	[62-66]	High-energy crushing and grinding	Increases the overall specific surface area of the minerals, i.e., the surface per unit mass available for Mg/Ca-extraction		
Thermal activation of the hydrated Mg-silicate serpentine [67–73] Heating the mineral to 630 °C or above		Destabilises the crystal lattice, thus increasing the reactivity of the mineral Heat activation also creates an even higher specific surface area [46]			
Increasing reaction temperatures [74,75] Applying operating temperatures above 100 °C			Accelerate the kinetics of the reaction		
Increasing reaction pressure [76,77] Applying operating CO ₂ pressure above 150 bar		Increases the activity of protons needed fo metal extraction. Also counteracts the low solubility of CO ₂ at high temperature			
Using organic and inorganic [61,78–80] Adding different substances as catalysts and additives to the reactants		Enhances the kinetics of the carbonation process and precipitation of magnesium carbonate			
Applying New double-step and multistep process designs	[81]	The operating conditions are changed between the different stages	Allows to control and promote extraction and precipitation separately		
Direct capture of CO ₂ from flue [81,82] gas stream		Capturing CO ₂ directly from a flue gas stream by mineral carbonation	Provides a simple and straightforward process route		

Table 1. Strategies and methods used to increase the speed and efficiency of the carbonation reaction.

Some of these and other papers are reviewed below. The literature on the use of basalt on the soil is also relevant since although the rate of dissolution of basalt is lower than that of olivine.

Bates and Morgan (1985) The rate of **chrysotile olivine** $(Mg_3(Si_2O_5)(OH)_4 \text{ asbestos})$ dissolution over five days was studied in constant-pH, batch suspensions at 25°C. After the first day, release of Mg occurred at a constant rate and exhibited a fractional dependence on pH,

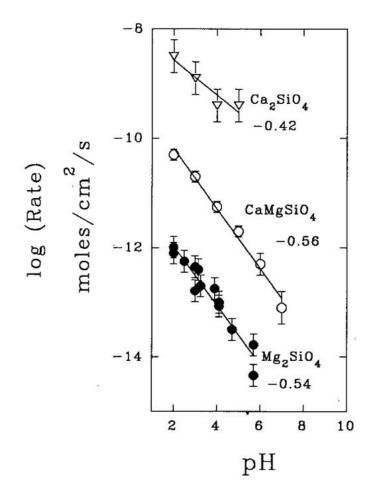
 $[H^+]^{(0.24)}$ interpreted in terms of a site-binding model for adsorption of protons on the surface. This fractional dependence implies that the rate is **limited by a chemical reaction involving less than one adsorbed proton per Mg released** into solution. The actual magnitude of the rate (10^{-15.7} mol/cm²/s at pH 8) supports this interpretation. The inorganics NO₃⁻, Cl⁻, HCO₃⁻ and SO₄⁻² and the organics catechol and oxalate affected the rate of Mg release only during the initial 12 to 24 hours of each experiment. Silica release was linear from the outset of each experiment but showed no definite pH dependence.

Seifritz (1990) In a brief note in *Nature*, Seifritz noted that the combination of CO₂ with calcium silicate is slightly **exothermic** while most other reactions are endothermic. Thus,

 $2CO_2 + H_2O + CaSIO_3 \rightarrow Ca^{2+} + 2HCO_3 + SiO_2 - 29.6$ kcal

He suggested that pressurized CO_2 could be pumped into a closed container containing a suspension of pulverized silicates in water. The resultant hard water and SiO₂ could be drained into the deep ocean and the process repeated. He felt that experimental work would be necessary to determine if this scheme was practical.

Westrich, et. al. (1993) examined the dissolution rates of three types of olivine varying by whether these silicates were complexed with Ca₂ or Mg₂ or intermediate CaMg. The dissolution rates by pH at 25°C are shown as follows.



Dissolution rate of Larnite olivine Ca₂SiO₄, Montecellite olivine MgCaSiO₄ and Fosterite olivine Mg₂SiO₄ by pH at 25°C.

Note the progressively more rapid dissolution rates progressing from Mg_2 to CaMg to Ca₂ silicates. The **dissolution rate of Larnite olivine**, Ca₂SiO₄, was 4 orders of magnitude faster than Fosterite olivine. If this is a common mineral it could be ideal for CO₂ sequestration EW.

Kojima et al, (1997) Proposed the absorption and fixation of CO₂ using calcium and magnesium silicates. The amounts of pulverization energy of wollastonite (CaSiO₃) and olivine sand were evaluated using industrial data of their pulverization. It was concluded that the CO₂ absorption by rock weathering was one of the most promising measures for the CO₂ problem.

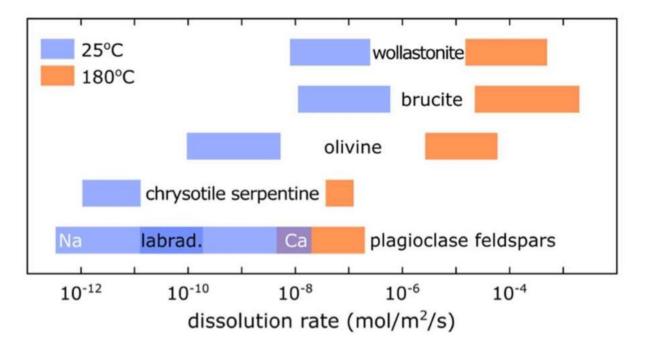
Jonckbloedt (1998) A kinetic model for the dissolution of olivine in sulphuric acid at elevated temperatures was presented. The effects of temperature, grain size fraction and olivine amount on the neutralization rate were quantified by carrying out a range of completeneutralization experiments. Under natural weathering conditions the dissolution rate of olivine was controlled by rates of surface reactions. Under these conditions dissolution was kinetically controlled by surface reactions. For the interpretation of the experimental data, a measure of the hydrogen ion activity was required. The equation used was validated for the dissolution of **Norwegian olivine**, with **grain sizes from 63 to 300 \mum**, in sulphuric acid at temperatures ranging from 60 to 90°C. These are quite large grain sizes.

Chen, et al (2000) Dissolution experiments with **forsteritic olivine** were conducted in a batch reactor at a temperature of 65°C between pH 2 and 5. As temperature increased, the dissolution rate of forsteritic olivine becomes more pH-dependent, which is consistent with **a** surface protonation model for dissolution (i.e., adding H⁺ to the surface). The activation energy of dissolution, E_a has been estimated based on their results and literature data at 30±4 kcal/mol.

Rosso and Rimstidt, (2000) The authors reviewed 10 studies of dissolution rates of olivine at up to 90 °C and a full range of pH. The **dissolution rates ranged from 1.3 x 10^{-11} to 7.6 x 10^{-13} mol/cm²/s**

Albany Research Center (ARC) (2000 to 2005). This pioneering work on CO₂ dissolution and mineralization of ultramafic rocks for the purpose of greenhouse gas emission control, included over 700 kinetic tests conducted at the Albany Research Center (ARC) in the US (now part of the National Energy Technology Laboratory) by O'Connor and coworkers. Much of this work was initially directed toward the extraction of Mg and improvement of *in situ* CO₂ storage, not the improvement of using ultramafic rocks on cropland. Nevertheless, these studies could have relevance to the latter.

The following diagram lets one get a feel for the values and units of different dissolution rates at two different temperatures.



Dissolution rates of magnesium- and calcium-rich minerals at 25 °C (blue) and 180 °C (orange). The plagioclase feldspars (NaAlSi₃O₈ to CaAl₂Si₂O₈) are a solid solution between a sodium-endmember (albite NaAlSi₃) and a calcium-endmember (anorthite CaAl₂Si₂O₈) indicated as **Na** and **Ca**. The most common plagioclase feldspar basalt is

labradorite (labrad.). Wollastonite = $CaSiO_3$. Brucite = $Mg(OH)_2$ Olivine = $(Mg,Fe)_2SiO_4$ Chrysotile serpentine = $Mg_3Si_2O_5(OH)_4$ (Figure from Kelemen et al, 2019) modified from National Academies of Sciences Engineering Medicine, NAS (2019).

The conditions of high temperature (180°C), high pCO_2 pressure (150 atm), and high salt concentrations play a role in the faster rates of dissolution compared to those quoted by other investigators.

O'Connor, W K O et al (2000). The ARC (Albany Research Center) (in Albany Oregon) have focused tests on *ex situ* mineral carbonation in an aqueous system. The process developed at ARC utilizes a slurry of water mixed with a magnesium silicate mineral, olivine [forsterite end member (Mg_2SiO_4) or serpentine ($Mg_3Si_2O_5(OH)_4$).

Results of the baseline tests, conducted on ground products of the natural minerals, have been encouraging. Tests conducted at ambient temperature (22°C) and subcritical CO₂ pressures (below 73 atm) resulted in very slow conversion to the carbonate. However, when **elevated temperatures and pressures** are utilized, coupled with continuous stirring of the slurry and gas dispersion within the water column, significant reaction occurs within much shorter reaction times. Extent of reaction, as measured by the stoichiometric conversion of the silicate mineral (olivine) to the carbonate, is roughly 90% within 24 hours, using distilled water, and a reaction temperature of 185°C and a partial pressure of CO₂ (PCO₂) of 115 atm. Recent tests using a bicarbonate solution, under identical reaction conditions, have achieved roughly 83% conversion of heat treated serpentine and 84% conversion of olivine to the carbonate in 6 hours. The results from the current studies suggest that reaction kinetics can be improved by pretreatment of the mineral, catalysis of the reaction, or some combination of the two. Future tests are intended to examine a broader pressure/temperature regime, various pretreatment options, as well as other mineral groups.

The focus of these experiments was an aqueous process using hydrochloric acid (HCl) to leach serpentine and produce magnesium chloride (MgCl₂). This reaction was well developed by the Tennessee Valley Authority and U.S. Bureau of Mines during World War II as part of an alternative process to produce **magnesium metal**. However, the complexity of this process led the ARC group to consider an alternative mineral carbonation process, the **direct carbonic acid route**, a new method for which DOE has filed a report of invention (O'Connor, et al., 1999).

In the **direct method** with carbonic acid, CO₂ is dissolved in a slurry of water and mineral reactant, such as **forsterite** (Mg₂ SiO₄). The CO₂ reacts with water to form carbonic acid (H₂CO₃), which dissociates to H⁺ and HCO₃⁻. Reaction of the carbonic acid with the mineral consumes most of the H⁺ and liberates equivalent amounts of cations (Mg²⁺) and bicarbonate (HCO₃⁻), which react to form the solid carbonate mineral **magnesite** (MgCO₃). Because this slurry is under high PCO₂, the carbonic acid is continuously regenerated as it is consumed, maintaining the reaction sequence until the mineral reactant is exhausted. The theorized reaction equation follows.

> $Mg_2SiO_4 + 2CO_2 + 2H_2O \Rightarrow 2MgCO_3 + H_4SiO_4$ Fosterite + Carbon dioxide + water = Magnesite + Silicic Acid

Several ultramafic complexes in North America contain enough magnesium silicate mineral to provide raw materials for the mineral carbonation of all annual CO₂ emissions for many years (Goff, et al., 1997).

Particle size was recognized as a major factor determining reaction rate and extent of reaction, because most mineral dissolution reactions are surface controlled. Initial carbonation tests conducted **on serpentine ground to -37 microns (37 um or less) resulted in much lower extent of reaction than identical tests conducted on olivine.** For example, when olivine was ground to -37 um, no pre-treatment, 185°C for 24 hours gave 91 **percent conversion**. When serpentine was treated the same way, it resulted in only 34 **percent conversion**.

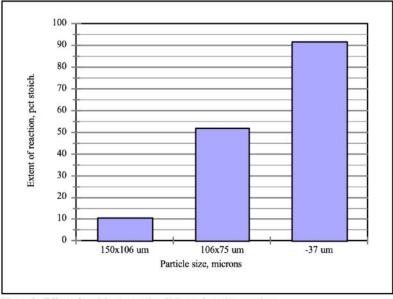


Figure 2.- Effect of particle size on the olivine carbonation reaction. Test conditions: 24 h, $T = 185^{\circ}C$, $P_{CO2} = 115$ atm, in distilled water.

The hydrated state of the serpentine was expected to have a negative impact on the carbonation results, so thermal gravimetric analysis (TGA) and differential thermal analysis (DTA) were conducted on the serpentine head sample to determine the appropriate temperature for removal of all water. The endotherms on the plot signify three separate stages of water removal. Desorption of adsorbed water was complete at 160°C, while evolution of water of crystallization (dehydration) was accomplished at 374°C. However, de-hydroxylation (evolution of constitutional water, or hydroxyl groups) required a temperature of 614°C. Subsequent heat treatments were conducted for 2 hours at 650°C, resulting in a consistent weight loss of 11 wt pct.

It was recognized that oxidation of the magnetite in the serpentine during heat treatment could potentially form a **passive layer of hematite** (Fe_2O_3) on the mineral surface, inhibiting the carbonation reaction. Thus, heat treatments were conducted in oxidizing (air) and non-oxidizing (CO₂) atmospheres to investigate this possibility. Analyses of the heat-treated products confirm that oxidation to hematite did occur in heat treatments conducted in air, while oxidation was limited during heat treatments conducted in CO₂. XRD analysis also confirms that the serpentine was transformed to forsterite because of the heat pretreatment.

The effect of the heat treatment on the **serpentine carbonation** reaction was minimal for the tests conducted in distilled water (see figure 5 below), although heat treatment in general improved the extent of reaction from 34% to over 57%. However, the effect of the heat treatment was significant for the carbonation tests conducted in the modified solution (0.5 M NaHCO₃, 1 M NaCl). Extent of reaction increased to over 83% for the **serpentine heat treated** in CO₂, compared to 41% extent of reaction for the serpentine heat treated in air; both results were achieved in just 6 hours. In fact, heat treatment of the serpentine in CO₂ resulted in an extent of reaction which virtually duplicated that achieved for olivine in the modified solution chemistry.

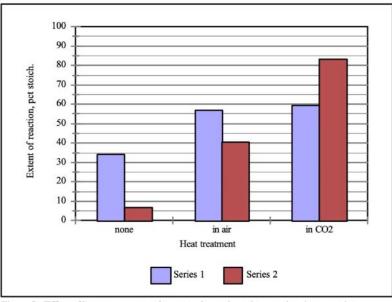


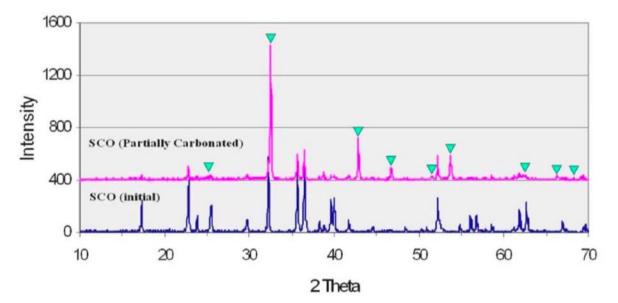
Figure 5.- Effect of heat treatment on the serpentine carbonation reaction, in two series: (1) 24 h, T = 185°C, $P_{CO2} = 115$ atm, in distilled water; and (2) 6 h, T = 185°C, $P_{CO2} = 115$ atm, in 0.5 M NaHCO₃, 1 M NaCl.

The results from these studies confirm that olivine and serpentine are equally amenable to the direct carbonation process, although **serpentine requires heat pretreatment**.

Béarat, H. e al (2003, 2006); McKelevy et al (2003) This study was from the Science and Engineering of Materials Graduate Program Arizona State University in Tempe. They pointed out that aqueous-solution olivine carbonation was **a complex process** associated with passivating silica layer formation and cracking, silica surface migration, olivine etches pit formation, transfer of the Mg and Fe in the olivine into the product carbonate, and the nucleation and growth of magnesite crystals on/in the silica/olivine reaction matrix. These phenomena occur in concert with the large solid volume changes that accompany the carbonation process, which can substantially impact carbonation reactivity.

The following **X-ray powder diffraction analysis** showed that the only crystalline product formed during mineral carbonation is magnesite, MgCO₃, resulting from the reaction of olivine with CO₂.

$$Mg_2SiO_4 + 2CO_2 \rightarrow 2MgCO_3 + SIO_2$$



The major product magnesite peaks are identified by the green triangles.

This suggest that this type of analysis could be used to follow the dissolution of olivine in field studies.

The sequestration reaction conditions were 1 M NaCl + 0.64 M NaHCO 3 at T \approx 185 °C and P CO₂ \approx 135 bar. A Large-scale atomic-level simulations of the reaction zone suggest that the silica rich passivating layer possesses a "glassy", but highly defective SiO₂ structure that can permit diffusion of key reactants. **Mitigating passivating layer effectiveness is critical to enhancing carbonation and lowering sequestration process cost.**

O'Connor, W.K.O. et al (2005). Aqueous mineral carbonation has been studied at the Albany Research Center as a potential option for CO_2 sequestration in collaboration with the Office of Fossil Energy - Mineral Carbonation Study Group of the DOE.

This research has included fundamental studies, resource evaluation, and process development. The studies have focused on the reaction of Ca, Fe, and Mg silicate minerals with gaseous CO₂ to form geologically stable, naturally occurring solid carbonate minerals. Process development has progressed in parallel with an economic evaluation, with an initial overall cost estimate of ~\$69/ton CO₂. Improved mineral pretreatment and reactor design indicate that costs could be reduced. However, the scale of *ex-situ* operations, requiring ~55 kt mineral/day to carbonate 100% of the CO₂ emissions from a 1 GW coal-fired power plant, may favor an *in-situ* methodology. Laboratory studies of *in situ* mineral carbonation showed promise.

The bench-scale grinding operations were conducted wet, to prevent dusting. Similar procedures would likely be necessary at the industrial scale.

This work has focused on the development of an *ex-situ* aqueous process to convert magnesium silicate-rich ultramafic rocks and minerals, such as **olivine**, **serpentine and basalt** to magnesium carbonates by contact with gaseous CO_2 in an aqueous solution. The output was in the form of stable carbonate compounds, such as calcite (CaCO₃), siderite (FeCO₃), and magnesite (MgCO₃). The carbonation reactions for the Mg²⁺, Ca²⁺, Fe²⁺ silicates are shown below.

$2Mg_2SiO_4 + CO_2 + 2H_2O \Longrightarrow Mg_3Si_2O_5(OH)_4 + MgCO_3$	Eq.1
$Mg_2SiO_4 + 2CO_2 + 2H_2O \Longrightarrow 2MgCO_3 + H_4SiO_4$	Eq. 2
$Mg_{3}Si_{2}O_{5}(OH)_{4} + 3CO_{2} + 2H_{2}O \Longrightarrow 3MgCO_{3} + 2H_{4}SiO_{4}$	Eq. 3

$$Fe_2SiO_4 + 2CO_2 + 2H_2O \Rightarrow 2FeCO_3 + H_4SiO_4$$
 Eq. 4

$$CaSiO_3 + CO_2 + 2H_2O \Rightarrow CaCO_3 + H_4SiO_4$$
 Eq. 5

A key theoretical yardstick for the value of a particular mineral reactant for mineral carbonation is its **carbonation potential.** The carbonation potential for a rock or mineral was described by Goff et al. (2000) regarding the hydrated magnesium silicate **serpentine** - Mg₃Si₂ $O_5(OH)_4$. Goff used the molar concentration of Mg in a serpentine sample to calculate the theoretical number of moles of CO₂ that could be converted to magnesite, MgCO₃, by reaction with the serpentine. The carbonation reactivity of a rock or mineral is dependent on numerous factors, including the mineral composition, pretreatment, and solubility at the specific carbonation conditions of time, temperature, and pressure.

This DOE study is one of the most comprehensive studies of the **relative carbonation potential**, **R**_{CO2}, **of different mafic minerals**. The following table shows these results. **R**_{CO2}, was calculated from the total molar concentration of Ca, Fe²⁺ and Mg in the feed, and is defined here as the **mass ratio of rock or mineral necessary to convert a unit mass of CO₂ to the solid carbonate**. By this definition, **a low R**_{CO2} **is preferable**. The reactivity of the various materials was measured as the **extent of reaction**, **R**_X, or the **percent stoichiometric conversion** of the Ca, Fe and Mg silicates to their carbonate counterparts. **A high Rx is preferable**. $\varepsilon_A =$ percent weight gain assuming 100% stoichiometric conversion of the available cations to the carbonates. The following Table 1 shows theses variables for the different compounds.

			Concentration, wt pct						
Rock/mineral			Feed Prod.		Prod.			1000	
group	Mineral	Formula	Ca	Fe ²⁺	Mg	CO ₂	R_{CO2}^2	ε _A , %	$R_x^{3}, \%$
Feldspar	Anorthite (An)	CaAl ₂ Si ₂ O ₈	10.3	3.1	4.8	1.9	4.4	23	9
Serpentine	Antigorite (Ant)	Mg ₃ Si ₂ O ₅ (OH) ₄	<0.1	2.4	24.6	24.2	2.1	47	92
Pyroxene	Augite (Aug)	$CaMgSi_2O_6 + (Fe,Al)$	15.6	9.6	6.9	11.1	2.7	37	33
Basalt	An, Aug, Mt, Ol		6.7	6.7	4.3	2.9	4.9	37	15
Olivine (Ol)	Fayalite (Fa)	Fe ₂ SiO ₄	0.6	44.3	0.3	19.2	2.8	36	66
Olivine (Ol)	Forsterite (Fo)	Mg ₂ SiO ₄	0.1	6.1	27.9	29.7	1.8	56	81
Serpentine	Lizardite (Liz)	Mg ₃ Si ₂ O ₅ (OH) ₄	0.3	1.5	20.7	16.0	2.5	39	40
Oxide	Magnetite (Mt)	Fe ₃ O ₄	0.6	21.9	0.3	1.5	5.5	18	08
Ultramafic	Talc	Mg ₃ Si ₄ O ₁₀ (OH) ₂	2.2	9.2	15.7	5.2	2.8	36	15
Ultramafic	Wollastonite (Wo)	CaSiO ₃	31.6	0.5	0.3	22.9	2.8	36	82

Table I. Mineral chemistry, carbonation potential, and reactivity.¹

¹ Carbonation test conditions: 80% -37 µm feed; 1 hour; 185°C; P_{CO2}=150 atm; 15% solids; 0.64 M NaHCO₃, 1 M NaCl.

² Mass ratio of ore necessary to carbonate unit mass of CO₂.

³ Reaction efficiency, percent stoichiometric conversion of Ca, Fe²⁺, and Mg cations in silicate feed to carbonate.

There is a great deal of important data in this table. Most of all, it answers the question of the relative value of serpentines such as antigorite to olivines such as forsterite and fayalite. The lower the Rco₂ and the higher the Rx, the greater that capacity to sequester CO₂. While the rate of dissolution of serpentines may be lower than olivines, the serpentine antigorite had the highest Rx 92, and the second lowest Rco₂ 2.1 of all the compounds

including the common Mg olivine Fosterite which had a Rx of 81, and a Rco₂ of 1.8 (the lowest). These studies indicate **that in addition to olivines, serpentines also qualify as excellent resources for EW.**

Second, these studies show the **wide range of ultramafic rocks that can be used for EW**.

Third, they show that even though ground up **basalt** has frequently been used for EW studies on croplands, it is among the least efficient in CO_2 sequestration of the ultramafic rocks listed.

This showed that the minerals with the **lowest** R_{CO2} were olivine as forsterite (1.8), olivine as fayalite (2.8). It is also important to note that serpentine as antigorite (2.1) and serpentine as lizardite (2.5) talc (2.8) and Wollasonite (2.8) also had low levels of R_{CO2} . Of interest basalt had the second highest R_{CO2} (4.9). These studies were carried out in aqueous media at elevated temperature (185 °C), elevated CO₂ pressure (150 atm) and elevated salts (0.64 M NaHCO₃ and 1 M NaCl).

How well these very abnormal conditions relate to carbonation of mafic minerals at ambient temperature and pressure on croplands are not known but the relative carbonation rates are probably relevant. **Pre-treatment consisting of fine grinding was important for olivine and serpentine.**

The ultramafic minerals investigated for mineral carbonation generally occur within large ophiolite complexes that are described as remnants of oceanic crust that have been compressed and folded along convergent continental margins. In North America, these ultramafic belts occur along both coasts, rather than the interior, which places some limitations on the application of EW to Midwest crops.

The conclusion of the ARC studies was that the following equation depicted the optimum conditions for carbonation of ultramafic rocks.

$$Mg_{2}SiO_{4} + 2CO_{2} \xrightarrow{\sim 185 \text{ °C}, \sim 150 \text{ atm } CO_{2}}{0.64 \text{ M NaHCO}_{3} \text{ 1M NaCl}} 2MgCO_{3} + SiO_{2}$$

These are clearly not suitable conditions for EW on soils. Thus, further studies were required.

Schuiling and Krijgsman (2006) The title of this article is: *Enhanced Weathering: An Effective and Cheap Tool to Sequester* CO_2 . The problem is how many others agree with this optimistic appraisal? He points out that weathering, until recently, has received little attention, although it is the most important way in which nature keeps the CO₂-levels in the atmosphere down. Mg olivine (Mg₂SiO₄) is an abundantly available magnesium silicate which weathers according to the reaction:

$$(Mg, Fe)_2 SiO_4 + 4 CO_2 + 4H_2O \Rightarrow 2(Mg, Fe)^{2++} 4 HCO_3 + H_4SiO_4$$

This formula indicates that 4 mol of CO_2 are sequestered by 1 mol of olivine, equivalent to **1.25 t** of CO_2 (or 0.34 t of C) per ton of olivine.

Olivine is a cheap and widely available material. By the authors calculations, to neutralize the CO₂ currently in the atmosphere, we need to spread a layer of olivine over the

whole surface of the earth at about 0.12 cm thickness. If we limit the olivine spreading to the land mass, the thickness of the layer would be 0.4 cm. This is a huge amount, equivalent to 1% of the total volume of rock moved by human civilization in its entire history, but even much smaller amounts of olivine could sequester substantial amounts of CO₂, every little bit helps.

In conclusion, they state that point sources of CO_2 such as coal generation of electricity, can be treated by reaction with reactive magnesium or calcium-silicates in autoclaves. The products, magnesium-carbonate or calcium-carbonate and precipitated silica should find application, in construction materials, and would make this process economically more attractive. In addition, since some of the **reactions with olivine produce heat**, this could be used constructively (Schuiling, 2006).

Since many parts of the world are still susceptible to acid rain, it is also possible to use the concept of enhanced weathering by applying powdered olivine or crushed basalt to farmland and woodland that are threatened by acid rain; **this is probably the cheapest way to sequester large volumes of CO₂**, while it provides at the same time an effective way of counteracting the effect of acid rain on forests and improving the quality of the forest soil.

In summary, the authors get their claim of a cheap tool by producing commercial products and mechanisms of protecting farmlands from acid rain. It still does not negate the huge amounts of olivine required and the expenses involved.

The following two papers are reports of studies by the McKelvey/Chizmeshya group supported by DOE grants and referred to as the **Arizona State University (ASU) studies.**

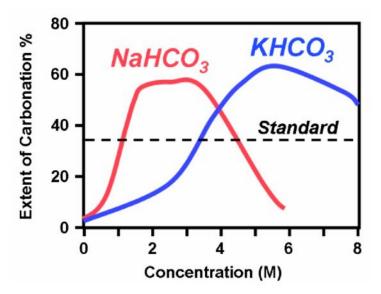
Chizmeshya, McKelvey, et al, (2004) Enhancing carbonation reactivity is key to economic viability of CO₂ sequestration. Recent studies at the U.S. DOE **Albany Research Center** have established that aqueous-solution carbonation using supercritical CO₂ is a promising process; even without olivine activation, 30-50% carbonation has been achieved in an hour. **Mechanical activation (e.g., attrition) has accelerated the carbonation process to an industrial timescale (i.e., near completion in less than an hour), at reduced pressure and temperature. However, this activation cost is too high to be economical and lower cost pretreatment options are needed.**

During the first project year they developed a new **sonication exfoliation** apparatus with a novel sealing system to carry out the sonication studies. They also initiated investigations to explore the potential that sonication may offer to enhance carbonation reactivity. During the second project year, they extended their investigations of the effects of sonication on the extent of carbonation as a function of the following parameters: particle size distribution, the mass of solid reactant, volume fraction of aqueous solution present, sonication power, time, temperature, and CO_2 pressure. To date, none of the conditions investigated have significantly enhanced carbonation.

By contrast, high concentration sodium, potassium, and sodium/potassium bicarbonate aqueous solutions have been found to be the most effective solutions for enhancing aqueous olivine carbonation to date. Thus far, they have succeeded in nearly doubling the extent of carbonation observed compared with the optimum procedure previously developed by the Albany Research Center.

The most promising solutions for enhancing carbonation to date have provided substantial increases in extent of carbonation, nearly doubling it. High concentrations of

NaHCO₃ (2.5M) and KHCO₃ (5.5M) were found to be particularly effective at enhancing carbonation, with the extent of carbonation again exhibiting a strong dependence on the alkali cation species present. As shown below, the NaHCO₃ was more effective at lower concentrations than KHCO₃.



Extent of carbonation of San Carlos Olivine as a function of NaHCO3 and KHCO3 concentration after 1h at 185°C, 2200 psi of CO₂ and stirring at 1,500 rpm. The dashed horizontal line represents the extend of carbonation using standard ARC conditions.

In their YEAR 2 studies they also demonstrated that the **addition of quartz particles** as an abrasive slurry component significantly enhanced carbonation, further substantiating the **importance of particle-particle abrasion in enhancing passivating layer exfoliation and carbonation.**

Their goal was to develop the understanding needed to engineer new low-cost carbonation processes that avoid the cost of pretreatment activation. The primary focus is on enhancing passivating layer exfoliation, which has the potential to substantially enhance carbonation without the need for pretreatment activation.

McKelvy, Chizmeshya et al (2006) Carbonation of the widely occurring mineral olivine (e.g., forsterite, Mg₂SiO₄) is a large-scale sequestration process candidate for regional implementation, which converts CO₂ into the environmentally benign mineral magnesite (MgCO₃). Mechanical activation (e.g., attrition, grinding) has accelerated the carbonation process to an industrial timescale (i.e., near completion in less than an hour), at reduced pressure and temperature. However, the activation cost is too high to be economical and lower cost pretreatment options are needed. Herein, they report their second-year progress was exploring a novel approach that offers the potential to substantially enhance carbonation reactivity while bypassing pretreatment activation.

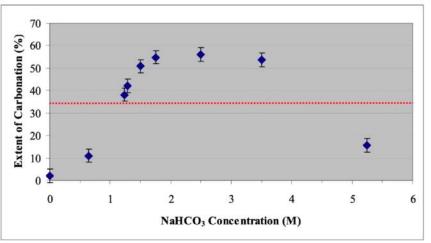
They discovered that **robust silica-rich passivating layers forms on the olivine surface during carbonation**. As carbonation proceeds, these passivating layers thicken, fracture, and eventually exfoliate, exposing fresh olivine surfaces during rapidly stirred/circulating carbonation. They tested incorporating select sonication to enhance exfoliation and carbonation. They succeeded in nearly doubling the extent of carbonation observed compared with the optimum procedure previously developed by the Albany Research Center.

Aqueous carbonation reactivity was found to be a strong function of the ionic species present and their aqueous activities, as well as the slurry fluid flow conditions incorporated. High concentration sodium, potassium, and sodium/potassium bicarbonate aqueous solutions have been found to be the most effective solutions for enhancing aqueous olivine carbonation to date.

Slurry-flow modeling using Fluent indicates that the slurry-flow dynamics are **a strong function of particle size and mass**, suggesting that **controlling these parameters may offer substantial potential to enhance carbonation**.

They developed a **new sonication exfoliation system** with a novel sealing system to carry out the sonication studies. They also initiated investigations into the potential that sonication offers to enhance carbonation reactivity. During the second project year, they extended their investigations of the effects of sonication on the extent of carbonation as a function of the following parameters: particle size distribution, the mass of solid reactant, volume fraction of aqueous solution present, sonication power, time, temperature, and CO_2 pressure. Thus far, none of the conditions investigated have significantly enhanced carbonation.

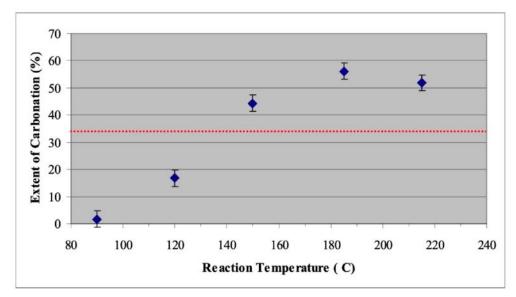
1,500 rpm stirring was used to replicate the ARC process in the studies at Arizona State University. These mineral carbonation reactions were performed using a 100 ml Autoclave Engineers EZE-Seal Hastelloy C-276 reactor, which is a smaller scale version of the 2,000 ml EZE-Seal Hastelloy C-276 reactor used at the Albany Research Center.



The results of the studies of the effect of NaHCO₃ are shown as follows.

Extent of carbonation of $< 38 \mu$ San Carlos Olivine as a function of NaHCO₃ concentration after 1h of carbonation at 185°C, under 2200 psi of CO₂, and with ~1500 rpm stirring. The dashed horizontal red line represents the extent of carbonation observed using the standard 0.64M NaHCO₃+ 1.00 M NaCl aqueous solution under the same reaction conditions.

The effect of temperature is shown below,

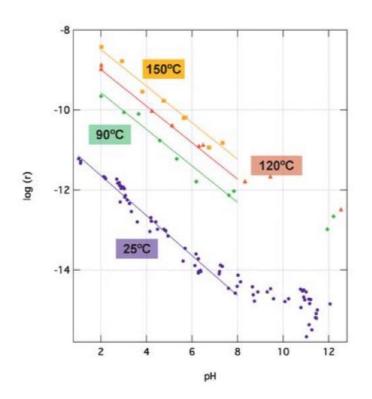


The effect of reaction temperature on the extent of carbonation of San Carlos olivine $(<38\mu)$. Reaction conditions: 1h, 2,200 psi CO₂, 1500 rpm stirring, and 2.5M NaHCO₃. The dashed red line represents the average extent of carbonation observed using the standard aqueous solution (0.64M NaHCO₃+ 1.00 M NaCl) at 185°C.

Studies during their no-cost extension period emphasized the impact that controlled aqueous speciation and activity and slurry-flow dynamics have on the mechanisms that control carbonation reactivity and the potential they offer to substantially reduce olivine mineral sequestration process cost.

Hänchen, M, et al (2006) examined the dissolution of olivine at temperature of 90 to 150° C in the presence of CO₂ at pressures of 15 to 180 bar. The presence of citric acid, an organic ligand, significantly increased dissolution rates in respect to the baseline HCl solution.

Prigiobbe, V. et al (2009) and Pokrovsky and Schott (2000). Looking for optimal conditions to speed up **dissolution of olivine**, experiments were performed in a flow-through reactor at 90-120-150°C. The pH was adjusted by adding either acids (e.g., HCl, citric acid) or LiOH, and by changing PCO₂. The salinity was changed by adding NaCl and NaNO₃. Here **r is the specific dissolution rate (mol/cm²/s)**.

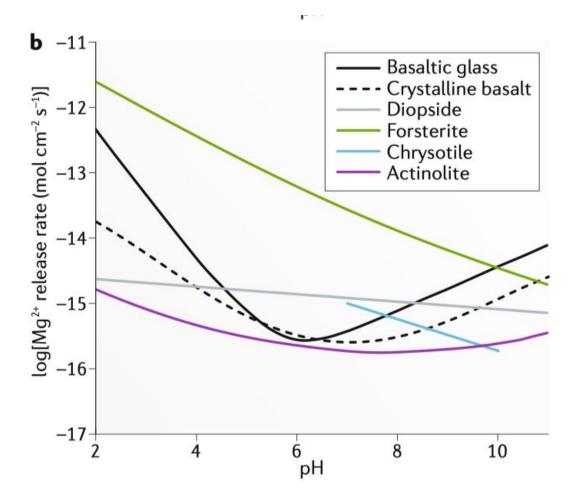


$\log(r) = -n \text{ pH } - E_{\text{A}}/(\text{RT}) + 0$
<i>T</i> = 150°C: log(<i>r</i>) = −0.46 pH − 7.58
<i>T</i> = 120°C: log(<i>r</i>) = - 0.46 pH - 8.07
<i>T</i> = 90°C: log(<i>r</i>) = - 0.46 pH - 8.66
<i>T</i> = 25°C: log(<i>r</i>) = - 0.50 pH − 10.64
el en el connect el

Logarithm of the specific dissolution rate r as a function of pH and at different temperatures. In **violet** is the literature data by Prokovsky and Schott (2000) for comparison.

Here it is possible to see the dissolution rate of Fosterite olivine at ambient temperature $(25^{0}C)$ and neutral pH, similar to that of soil. At neutral pH the dissolution rates are 10^{-14} mol/m²/s. Lower pH and higher temperatures significantly increased the dissolution rates. While these studies were designed for capture of CO₂ from flu gas the data for neutral pH and ambient temperature have some relevance to the application of olivine to soil.

Snæbjörnsdóttir et al (2020) As a comparison with the above figures, this author compared the dissolution studies of different minerals by several authors.



Calcium and magnesium release rates from mafic rocks and minerals. Variation of Mg^{2+} release rates from common minerals at pH, 25 °C. chrysotile = $Mg_3(Si_2O_5)(OH)_4$; basaltic glass; diopside = $MgCaSi_2O_6$; crystalline basalt, forsterite = Mg_2SiO_4 actinolite = $Ca_2(Mg_{4.5-2.5} Fe^{2+}_{0.5-2.5})S_{i8}O_{22}(OH)_2$. See paper for references.

Note that forsterite olivine dissolution has a steep linear relationship to pH while diopside have an almost flat relationship. The important lesson is that **some mafic and ultramafic rocks do not have a strong relationship to pH.** There was good agreement with the dissolution rate of forsterite vs pH between Prokovsky and Schott (2000) (above) and the Snæbjörnsdóttir et al (2020) data.

Renforth, (2012) The silicate resources in the UK are large and could theoretically capture **430 billion tons (Gt) of CO₂.** Most of this resource is contained in basic rocks (with a **carbon capture potential of ~0.3 tCO₂/t rock**). There are a limited number of ultrabasic formations (0.8 tCO₂/t rock) with a total carbon capture potential of 25.4 GtCO₂. It is shown that the energy costs of enhanced weathering may be 656–3501 kWh/tCO₂ for basic rocks and 224–748 kWh/tCO₂ for ultrabasic rocks. **Grinding and transport are the most energy intensive processes accounting for 77–94% of the energy requirements collectively**. The operational costs of enhanced weathering could \$70–\$578/tCO₂ and \$24–\$123/tCO₂) for basic and ultrabasic

rocks respectively. Providing sufficient weathering rates full exploitation of this resource is not possible given the environmental and amenity value of some of the rock formations. Furthermore, the weathering rate and environmental impact of silicate mineral application to the land surface is not fully understood, and further investigation in this area is required to reduce the uncertainty in the estimated costs presented here.

Turianicová, E. et al (2013) studied the influence of mechanical activation of olivine on the carbonation process at ambient temperature $(25 \pm 1 \text{ °C})$ and at significantly lower pressure than in previous work (60 bar), and no organic or inorganic additives were added to enhance the process. Structural, surface, and morphological changes of mechanically activated olivine resulted in an increased reactivity. The process produced **amorphous magnesium** carbonate in the form of hydromagnesite ((MgCO₃)₄ ·Mg(OH)₂ ·4H₂O) which is energetically favored over magnesite (MgCO₃). The authors proposed that the mineral carbonation of mechanically activated olivine proceeds according to a reaction forming hydromagnesite.

Moosdorf, N. et al (2014) concluded that **terrestrial enhanced weathering consumes more CO₂ than it emits for mining, comminution, transport, and application in most locations.** The CO₂-efficiency is dominated by the choice of source rocks and material comminution. CO₂ emissions from transport have a small effect on the overall budget (on average 0.5-3% of potentially sequestered CO₂ and the emissions of material mining and application are negligible. After all emissions, **0.5-1.0 t CO₂ can still be sequestered on average per ton of rock**. However, very large amounts of rock would be needed to control or reduce the atmospheric CO₂ concentrations substantially with enhanced weathering. Before enhanced weathering could be applied at large scales, more research is needed to assess weathering rates, potential side effects, social acceptability, and mechanisms of governance.

Soldal (2015) The emphasis in this study is the role of olivine weathering in combating the low pH-based release of N_2O . In this regard olivine, nepheline syenite and norite gave the highest pH increase of the silicates.

Strawn, Bohn, & O'Connor (2015) are the editors of the 4th edition of *Soil Chemistry*. Chapter 6. Mineralogy and Weathering Process in Soils presents the following table (6.8) showing the types of crystalline structure for different mafic and ultramafic rocks.

Classification (group)	Structural arrangement	Si/O ratio	Examples
Nesosilicates (island silicates)	Single tetrahedra	1/4	Olivine ((Mg,Fe) ₂ SiO ₄), garnet
Inosilicates (single-chain silicates)	Continuous single chains of tetrahedra sharing two corners	1/3	Pyroxene (MgSiO ₃)
Inosilicates (double-chain silicates)	Continuous double chains of tetrahedra sharing alternately two and three oxygens	4/11	Amphiboles $(Mg_{3.5}Si_4O_{11}(OH)_1)$
Phyllosilicates (sheet or layer silicates)	Continuous sheets of tetrahedra each sharing three oxygens	2/5	Micas, clay minerals (muscovite-K ₂ Al ₄ Si ₆ <u>Al</u> ₂ O ₂₀ (OH) ₄)
Tectosilicates (framework silicates)	Continuous framework of tetrahedra each sharing all four oxygens	1/2	Quartz, feldspars, zeolite (quartz-SiO ₂ ; orthoclase-K(Si ₃ <u>Al</u> O ₈)

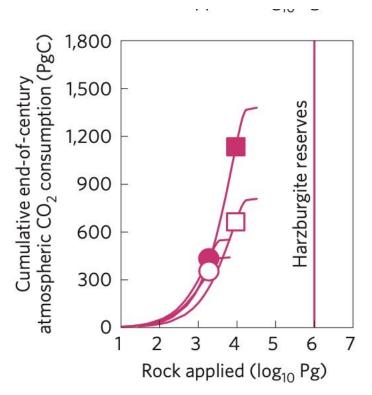
Table 6.8 Structural classification of silicates. The Si:O ratio refers to the number of Si atoms divided by the number of O atoms that are ligands in the Si tetrahedra. In determining Si:O ratio, isomorphic substitution of AI^{3+} in the Si⁴⁺ positions (underlined AI in table) counts as a silicon atom.

Olivine is a Nesosilicate with a single tetrahedra while the pyroxenes are Inosilicates with chains of tetrahedra and serpentines are Phyllosilicates with continuous sheets of tetrahedra each sharing three oxygens. These structures can account for the different dissolution rates of these minerals. The 3-D structures of olivine and serpentine are shown on other pages.

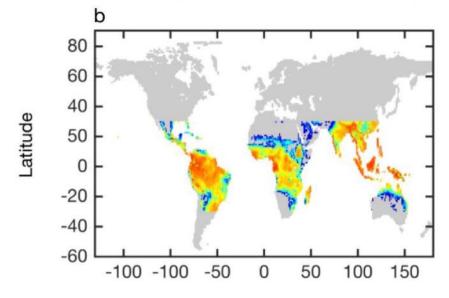
Kleiv et al, (2016) reported milling experiments on olivine combining the two milling modes, dry and wet. These were performed using a laboratory planetary mill. The specific surface area of the milled products was determined by N₂-adsorption (BET), and their crystallinity was studied using X-ray diffraction (XRD). Combining dry mechanical activation with subsequent wet milling made it possible to produce specific surface area at rates that exceed those that can be obtained by wet milling alone. A value of $26.28 \pm 1.28 \text{ m}^2/\text{g}$ was obtained after 30 min of wet milling. By contrast, 25 min of dry mechanical activation followed by 5 min of wet milling resulted in a specific surface area of $64.44 \pm 2.13 \text{ m}^2/\text{g}$. The concept could represent significant energy savings. This may have relevance to grinding serpentines.

Taylor et al (2016) In one of the few articles that **take advantage of the striking increase in weathering of olivine type rocks in moist, tropical regions and weathering hotspots**. They found that enhanced weathering scenarios over less than a third of tropical land could significantly draw down atmospheric CO₂ and ameliorate ocean acidification by 2100. However, they emphasize the problems with cost, acceptance, and potential unanticipated side effects.

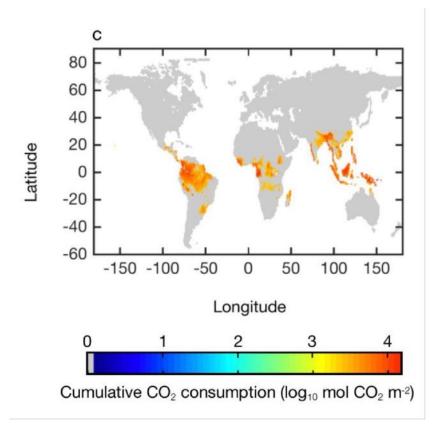
They examined the use of three minerals: **Dunite** (olivine – $(Mg-Fe)_2 SiO_4$, **Harzburgite** (olivine + low Ca⁺⁺ pyroxene) and **Basalt**. The results for Harzburgite were as follows:



This showed the **simulation** of the application of Harzburgite. Squares represent application in square plots and circles the application in circular plots. The **red squares and circles represent limitation of Harzburgite to Tropical Weathering Hot Spots**. The white squares and circles represent application of Harzburgite to all tropical areas. At a level of application of 4 Pg of Harzburgite there was a sequestering of 1,150 Pg of carbon. The vertical line labeled Harzburgite indicates there were adequate reserves of the mineral.

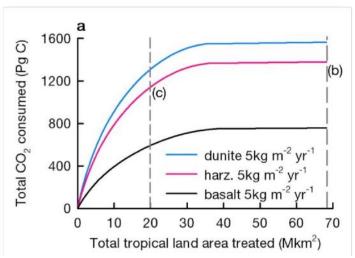


This is a map of the total tropical area 30^0 N to 30^0 S. It include both the tropical weathering hot spots and non-hot spots.



This is a map of the **Tropical Weathering Hot Spots** illustrates the meaning of this term, namely **areas where the cumulative CO₂ consumption is between 3 and 4 10g₁₀ mol CO₂/meter.**

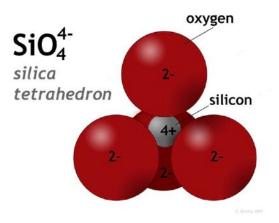
The next figure summarizes all the above.



In this diagram of simulations, the vertical line **b** represents how much of each mineral is deposited over the entire tropics consisting of both hot spots and non-hot spots. The vertical line **c** how much of each mineral was deposited **only on hot spots** representing 20 Mkm². Their

conclusion was that over 80% of the total CO₂ consumption could be obtained by restricting the application to 5 kg/m² of harzburgite per year to the hot spots. This suggests that the 29-fold greater Enhanced Weathering in tropical wet climate than in temperate dry regions needs to be multiplied by 5, or 145 times to compare temperate dry regions to tropical hot spots.

Oelkers et al. (2018) Olivine dissolution reactivity is relatively simple. Its structure is comprised of isolated Si-O⁴ 4-tetrehedra (Neosilicate) linked by divalent cations.



Aqueous species that adsorb to these bonds apparently accelerate their destruction. For example, the absorption of H^+ , H_2O and, at some conditions, selected aqueous organic species will increase olivine dissolution rates. Nevertheless, other factors can slow olivine dissolution rates. Notably, olivine dissolution rates are slowed by lowering the surface area exposed to the reactive aqueous fluid, by for example the presence and/or growth on these surfaces of either microbes or secondary phases.

A survey of the literature suggests that the major factors influencing forsterite olivine dissolution rates are **pH**, water activity, temperature, and surface area. Evidence suggests that the effects of aqueous inorganic and organic species are relatively limited and may be attributed at least in part to their influence on aqueous solution pH. Moreover, the observed decrease in rates due to the presence of secondary mineral coatings and/or the presence of microbes can be attributed to their ability to decrease olivine surface area directly exposed to the reactive aqueous fluid.

Olivine dissolution can proceed by the breaking of just the ionic Mg-O bonds, liberating the SiO⁴⁻ anions directly into solution. **Due to both the absence of covalent Si-O-Si bonds and the relative weakness of the ionic divalent metal-oxygen bonds in its structure, olivine is among the fastest dissolving silicate minerals.**

II. Olivine Dissolution: Field Studies on Cropland or Simulated Field Studies

The one thing that became obvious is that there are very few actual field studies of EW.

ten Berge et al (2012) The author's objectives were to assess weathering of olivine in soil, and its effects on plant growth and nutrient uptake. In a **pot experiment** with perennial ryegrass (*Lolium perenne* L.), weathering for 32 weeks, was inferred from bioavailability of magnesium (Mg) in soil and plant. Olivine doses were equivalent to 1,630, 8,150, 40,700 and 204,000 kg/ha. Olivine increased plant growth (+15.6%) and plant K concentration (+16.5%). At all doses, olivine increased bioavailability of Mg and Ni in soil, as well as uptake of Mg, Si and Ni in plants. Olivine suppressed Ca uptake. Weathering appears fast enough to support the EW concept. Olivine amounts must remain within limits to avoid imbalances in plant nutrition, notably at low Ca availability and to avoid Ni accumulation in soil and crop.

Renforth et al (2015) Despite considerable work in recent decades, significant gaps in understanding natural weathering remain. **Dissolution rates determined from catchment scale investigations are generally several orders of magnitude slower than those predicted from kinetic information derived from laboratory studies.** Based on these laboratory studies, temperature, mineral saturation, pH, and **surface area** are important variables. **In soil rainfall rate is also important.**

The authors presented results from **laboratory flow-through dissolution experiments** which seek to bridge this observational discrepancy by **using columns of soil returned to the laboratory from a field site**. Continual addition of water to the top of the soil columns, and analysis of elemental composition of waters exiting at the base was conducted for a **period of five months**, and the solid and leachable composition of the soils was also assessed before and after the experiments. Chemical results indicate clear release of Mg⁺² from the dissolution of olivine and, by comparison with a control case, allow the **rate of olivine dissolution to be estimated between 10**^{-16.4} **and 10**^{-15.5} **moles (Mg)/cm²/s.** This is based on the Olsen (2017) and TNO (2008) model of the rate of dissolution. The olivine dissolution rates are intermediate between those of pure laboratory and field studies and provide a useful constraint on weathering processes in natural environments, such as during soil profile deepening or the addition of mineral dust or volcanic ash to soils surfaces.

Several workers have suggested that the release of potentially toxic elements during the dissolution of olivine may pose an environmental risk which would subsequently lower the potential of terrestrial enhanced weathering (Hartmann et al., 2013; Renforth, 2012). From the results of this study, there was elevated Cr in five of the solution samples from the olivine column, the remaining samples showed no difference compared to the control. Ni was measured but was below the detection limit in all the effluent solutions.

This suggests that >99% of these trace elements are retained within the soil, which is unsurprising given the high concentration of these elements in very mature soils such as laterites (Lewis et al., 2006), implying that the short-term environmental impact of trace metals from the added olivine may be limited. However, the long-term accumulation of these elements may pose an environmental risk, which could eventually limit the application.

The largest uncertainty is the energy requirements of material pulverization. (Renforth, 2012). Simple calculations indicate that it would be necessary to grind olivine to a particle size of 1 um or less to enable dissolution in 1–5 years, requiring grinding energy of around **1.5 GJ (electrical) per ton of rock** (comparable with the more extensively studied alternatives for CO₂ uptake such as direct air capture). Setting up renewable energy sources could divert these costs.

Dietzen, C. et al (2018) Applying **finely ground silicate minerals to soils** could mitigate CO₂ emissions by enhancing the rate of carbon sequestration via silicate weathering. Using these minerals instead of agricultural lime to increase soil pH would also **eliminates the dissolution of lime as a major source of agricultural CO₂ emissions.** However, dissolution rates of silicate minerals in the soil environment are uncertain and the impacts of their application on the decomposition of soil organic matter have yet to be determined. A **3-month soil incubation** was performed to investigate the **effects of olivine**, a highly weatherable silicate mineral, **at two application rates, OLIVIow (0.008 g/g soil) and OLIVhigh (0.04 g/g soil)**. There was no difference in cumulative net CO₂ flux between the olivine-amended soils and the control though **total flux from the lime soils was 221% higher than the control.** Heterotrophic respiration was also greatest in the lime-amended soils. The weathering rate of OLIV low (26.7%) was higher than of OLIV high (7.1%), but **both treatments increased soil pH to a level sufficient to overcome aluminum toxicity**. Their results suggest that **olivine amendments are an effective tool for carbon sequestration and a suitable replacement for lime**.

Kelektsoglou, K. (2018) aimed to provide the current state-of-the-art of CO_2 capture, transport, and storage focusing on mineral carbonation, based on the reaction of CO_2 with calcium or magnesium oxides or hydroxides to form stable carbonate materials. Currently in Europe only three commercial scale DACS projects are in operation while twenty-one of them are in pilot phase, including the only case of mineral carbonation in Europe i.e., Carbfix in Iceland. The author considers the necessity of CO_2 sequestration in Greece where there are currently emissions of about 64.6 million tons of CO_2 produced annually, originating from the lignite fired power plants. They demonstrated the potential applicability of several geological sites around Greece for mineral carbonation such as Mount Pindos and Vourinos **ophiolite complexes**.

Amann, et al (2020) Instead of covering a large tract of cropland, Amann et al **Enhanced Weathering and related element fluxes** – a cropland mesocosm approach, chose to use vary small plots of soil, thus the term a mesocosm approach. They stated that while there are some studies that propose and theoretically analyze the application of rock powder to agricultural land, results from field experiments are still scarce.

To evaluate the efficiency and side effects of Enhanced Weathering, a mesocosm experiment was set up and agricultural soil from Belgium was amended with **olivine-bearing dunite ground to two different grain sizes**, with and without crops.

Based on measurements of Mg, Si, pH, and DIC, the additional weathering effect of olivine could be confirmed. Calculated weathering rates are up to 3 orders of magnitude lower than found in other mostly laboratory and theoretical studies. The calculated CO₂ consumption by weathering based on the outlet water of the mesocosm systems was low with 2.3–4.9 tCO₂/km²/yr if compared with previous theoretical estimates. Suspected causes were the removal or dilution of Mg as a weathering product by processes like adsorption, mineralization, plant uptake, evapotranspiration, and/or preferential flow, not specifically addressed in previous EW experiments for CO₂ consumption. The observation that Mg

concentrations in the upper soil layers were about 1 order of magnitude higher than in the outlet water indicates that a careful tracking of weathering indicators like **Mg in the field is essential for a precise estimate of the CO₂ consumption potential of EW**, specifically under global deployment scenarios with a high diversity of ecosystem settings. Porewater Mg/Si molar ratios suggest that dissolved Si is reprecipitating, forming a cation-depleted Si layer on the reactive mineral surface of freshly ground rocks.

The release of potentially harmful trace elements is an acknowledged side effect of EW. Primarily Ni and Cr are elevated in the soil solution, while Ni concentrations exceed the limits of drinking water quality. The use of olivine, rich in Ni and Cr, is not recommended, and alternative rock sources are suggested for the application.

While the kinetics are relatively well understood at the laboratory scale, the dissolution rate of a rock powder mixture as soil amendment, with fresh surfaces, which have not been in contact with an aquatic phase before, is nearly unknown. Several points of the rock powder application on soils have to be considered.

First, the upper parts of soils are not permanently saturated with water, which may lead to mineral dissolution-precipitation reactions.

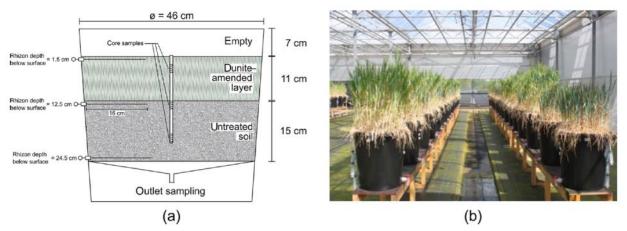
Second, it can be expected that mineral surfaces initially need to equilibrate with the new system and varying water content and that dissolution rates of minerals will be different from those in long-term equilibrium within the natural soil system.

Third, trace elements from the applied rock material will eventually be released and migrate downwards, reprecipitated if oversaturation with a specific mineral phase occurs, or adsorbed to soil minerals or organic matter.

They studied the release of the major elements Mg and Si predominantly derived from Mg olivine, as indicators for the inorganic CO₂ sequestration potential, and assessed whether the release of elements into the soil solution occurs stoichiometrically, or whether a secondary layer covering the fresh surfaces of minerals will develop, potentially enriched in Si and depleted in Mg (Daval et al., 2013a; Hellmann et al., 2012; Pokrovsky and Schott, 2000), which could influence weathering and subsequently sequestration rates. In addition, the release of trace metals was used to understand how these behave in a near-natural environment to evaluate the impacts on the environment.

Methods. Rain barrels were used as miniature growing sites (mesocosms). They had a diameter of 46 cm and were filled with a natural loamy sandy soil from Belgium. Olivine-rich dunite was added to the top layer of the soils at a rate of 22 kg/m^2 . Two different grain sizes were used – course and fine. It was applied to two crops, wheat, and barley, and two different irrigation regimes, daily and weekly. Controls consisted of barrels without added dunite, and barrels without plants.

Soil material was obtained by extracting sediment cores (20 cm long and 28 mm in diameter) using a hammer auger with a removable plastic lining (Eijkelkamp 04.15.SA foil sampler, Giesbeek, the Netherlands). The following figures shows a summary of the methods.



(a) Schematic mesocosm configuration; (b) status of the experiment in April 2014 (6 months in).

Vinita, R (2020). In this rather pessimistic report, the overall potential of EW depended on the availability of suitable rocks and proximity to the spreading locations. The potential and environmental implications of enhanced weathering of olivine in arable lands of Europe was studied. The research objective is to mitigate 10% of EU's 2017 total CO₂ emissions by 2050, with the mineral sourced from the biggest olivine quarry in Norway. Dunite in this quarry has high purity (~92%) of olivine, which has high dissolution reactivity. The accumulation of nickel in the topsoil was investigated. Scenarios were made for selected countries in Europe (northern and southern Europe) and most European countries. It was found that, for European scale, the current mining production in Norway needs to be increased 500-1000 times to achieve the target. Suitable pH soil for terrestrial ESW is 5-7, and 75 µm and 30 µm were chosen based on the shrinking core model. At soil pH of 7-8, weathering can still proceed, although it requires 10 µm grain size for a considerable weathering amount, e.g., 70-80% weathered in 25 years. This was proven to be highly inefficient, resulting to more CO₂ being emitted than sequestered. Of all the mechanical processes involved to spread grounded olivine on arable land, transport contributed to the highest reduction of CO2 potential. However, fast weathering rates are found in countries with higher mean annual temperature, which are remotely located from the source. All scenarios meeting the targets also resulted to substantial amount of nickel accumulation in the topsoil by 2050. These amounts exceed the Dutch's maximum permissible addition (MPA) value of 0.26 mg Ni/kg topsoil. However, this is dependent on the weathering rate, which differs strongly by geographical locations. Overall, the main uncertainties were in the weathering rate.

Von Strandman, et al (2021) This study presents lithium and magnesium isotope **ratios of soils** and their drainage waters from a well-characterized weathering experiment with two soil cores, one with **olivine added to the surface layer**, and the other a control core. The experimental design mimics olivine addition to soils for CO₂ sequestration. At the start of the experiment, waters draining both cores have similar Mg isotope composition to the soil exchangeable pool. The composition in the two cores evolve in different directions as olivine dissolution progresses.

For Li, waters exiting the base of the cores initially have the same isotope composition, but then diverge as olivine dissolution progresses. For both Mg and Li, the transport down-core is significantly retarded and fractionated by exchange with the exchangeable pool. This observation has implications for the monitoring of enhanced weathering using trace elements or isotopes, because dissolution rates and fluxes will be underestimated during the time when the exchangeable pool evolves towards a new equilibrium.

How Much Rock is Required per Ton of CO₂ sequestered? The ability to sequester atmospheric CO₂ is material specific and depends on the Mg²⁺ that can be released during hydrolysis from the Mg-rich olivine. It is defined as the **carbon dioxide removal (RCO₂) in metric tons of CO₂ per metric ton of Mg olivine (estimated to be 1.1 for ultramafic (i.e., Mg rich) rocks**; Moosdorf et al., 2014). This assumption considers that impurities (like Fe abundance), in contrast to the ideal Mg olivine and equilibration effects, reduce the theoretical maximum RCO₂ of 1.25 for forsterite. Based on the average of Mg concentrations in the outlet water over the first year (340 d), the experiment leads to a **total annual CO₂ sequestration of** 2.3–4.9 t/tCO₂/km²/yr depending on the applied grain size. These **amounts are considerably** higher than some earlier estimates.

III. Serpentine Dissolution: Laboratory Studies

While the dissolution of olivine on croplands has been emphasized, the problem is that **most ultramafic rocks in the world are serpentized and the rate of dissolution of serpentine is significantly slower than that of olivine** (Daval, 2013). Some serpentine results were presented in Section I.

As to the question of whether serpentinized rock can be used for enhanced weathering on cropland, very few field studies have been undertaken about this. We believe it will work since basalt on cropland has been shown to work and the dissolution rate of basalt is slower than for serpentine.

Several things have been tried to accelerate the dissolution of serpentine. Much of that literature was aimed at the commercial extraction of magnesium, or use in extracting CO_2 from flu gas, while our goal is the relative rate of dissolution of serpentines in the soil. Most of the techniques proposed for the extraction of magnesium from serpentine would add significant costs to the use of serpentine on soils.

The serpentine group of minerals consists of the three polymorphs lizardite, antigorite, and chrysotile. The serpentine minerals are phyllosilcates, or sheet silicates, and share the general formula $Mg_3Si_2O_5(OH)_4$. As serpentine dissolves carbon dioxide is consumed by the reaction (Park and Fan, 2004)

 $Mg_3Si_2O_5(OH)_4 + 3CO_2 + 2H_2O \rightarrow 3MgCO_3 + 2SiO_2 + 4H_2O$

General formula for the serpentines is Mg,Fe,Ni,Al,Zn,Mn)₂₋₃ (Si,Al,Fe)₂O₅(OH)₄. The serpentine clay minerals are Lizardite, Atlantisite and Infinite, with the chemical composition of Mg₃Si₂O₅(OH)₄. They differ in color and where they are found. Lizardite is the most common and most often used in research studies.

Olivine is a nesosilicate mineral with the general formula $(Mg,Fe)_2SiO_4$. The olivine group consists of forsterite (Mg_2SiO_4) and fayalite (Fe_2SiO_4) . Olivine dissolves quickly in comparison to other silicate minerals. At earth surface temperatures, olivine dissolution usually occurs stoichiometrically and few weathering products are formed. The general reaction for olivine, specifically forsterite, dissolution is:

 $Mg_2SiO_4 + 4H_2CO_3 \rightarrow 2Mg^{2+} + H_4SiO_4 + 4HCO_3^{-}$

The studies of the dissolution of serpentines are reviewed below.

What is the most effective method of enhancing the carbonation of serpentines?

Luce at al., (1972) Kinetic dissolution experiments on serpentine, forsterite, and enstatite over a wide pH range at 25°C showed that there was an initial rapid exchange of surface magnesium ions with hydrogen ions followed by a longer period of hydrogen exchange and extraction of internal magnesium and silicon, with the amount extracted proportional to time. The diffusion coefficients decrease in the order forsterite > serpentine > enstatite (Mg,Fe)SiO₃).

Eventually the parabolic exchange rates decrease to the rate of dissolution of all material at the aqueous interface. Hence, over very long periods the amount of silicon and magnesium dissolved is proportional to time and dissolution is congruent. In highly acid solutions dissolution rates are fast and this terminal condition is reached much sooner.

Lin and Clemency (1981) Dissolution experiments were done on a series of layer-type Mg minerals (brucite, antigorite, talc, and phlogopite) of progressively more complex structure and chemical composition. Brucite Mg(OH)₂, Anigorite (Mg,Fe²⁺)₃Si₂O₅(OH)₄, talc Mg₃Si₄O₁₀(OH)₂, Phlogopite KMg₃AlSi₃O₁₀(F,OH)₂.

The advantages of this study were that dissolution was done in **water at room temperature and conditions**. A further almost unique advantage was that it examined **small particle sizes** with 9 groups from < .5 um to 37 ums. However, they were not studied individually but rather showed the range of particle sizes. For example, 35% of the anigoite sizes were less than 8 ums.

It appears that **the solubility of these layer-type minerals was related to the relative number of octahedral to tetrahedral sheets present in the structure**, i.e., the dissolution kinetics of layer-type silicate minerals is controlled by the rate of destruction of the tetrahedral silica sheets of the mineral.

Goff, F. and Lackner, K.S. (1998) Serpentinites and **dunites** comprise the best ores for CO₂ sequestration because they contain the most Mg by weight (35 to 49 wt-% MgO) and are relatively reactive to hot acids such as HCl. **Small ultramafic bodies (about 1 km³) can** potentially sequester about 1 gigaton of CO₂ or 20% of annual U.S. emissions. A single large deposit of dunite (30 km³) could dispose of nearly 20 years of current U.S. CO₂ emissions.

The **carbonation of serpentinite** is broken up into several steps. The mineral ore is mined and **ground to a powder**. To improve the carbonation reaction kinetics, the magnesium is extracted from the ore and put in the form of magnesium hydroxide. The extraction is **accomplished with HCl**, which dissolves the mineral forming MgCl₂, and silica, which is readily precipitated. This process was described in the 1940s and 1950s when Mg shortages were driving research into alternative extraction technologies. This is a complex process initially designed for the extraction of magnesium and involving piping CO₂ and Mg(OH)₂.

Drief and Nieto (1999) reported that with prolonged grinding the crystal structure of the serpentine rock, antigorite, was affected mainly along the c axis, causing a partial loss of crystallinity. Vibration grinding modified mineral dehydration, accelerating the dehydroxylation process and transforming the structural OH to adsorbed water. The amorphous material product after 120 min showed the same composition as the initial antigorite. Grinding led to a general decrease in particle size at the beginning of the experiment followed by the agglomeration of ultrafine particles as grinding proceeded. Grinding seems to be an important process for water extraction, including structural water, thus accelerating the dehydroxylation process.

Kim and Chung, (2002) A serpentine mineral was treated in a planetary ball mill, and the effect of grinding was studied on the crystalline structure, average size, and metal extraction rate by sulfuric acid leaching. The crystalline peaks of the serpentine were gradually reduced with increase of grinding time, and after 120 min the serpentine turned into the amorphous phase. It was found that the extraction rate of the metals contained in the mineral by sulfuric acid was rapidly increased by the mechanochemical treatment. For the mineral treated for 240 min, Mg and Fe metal elements were extracted at 100% within 5 min.

Park and Fan, (2004). The effect of the physical activation on the dissolution of serpentine was investigated and a pH swing scheme was developed to improve the overall conversion of the CO₂ mineral sequestration process. Various methods of the surface agitation such as ultrasound and internal (in-situ) grinding were examined for their effectiveness in removing the diffusion limiting SiO₂ layer to promote further dissolution of the inner MgO layer of serpentine. It was found that the fluidization of the serpentine slurry with 2 mm glass beads was most effective in refreshing the surface of the serpentine particles during the dissolution process. Unlike the external attrition grinding, this method could be much less energy intensive. It was also found that the mechanical agitation via the internal grinding alone did not enhance the dissolution of serpentine, while the combination of the internal grinding and Mg leaching solvent resulted in rapid serpentine dissolution. Using the proposed pH swing scheme, the overall conversion of the mineral carbonation radically improved. By controlling the pH of the system, three solid products were generated from the mineral carbonation process: SiO₂-rich solids, iron oxide and MgCO_{3*3H2}O. Since the iron oxide and MgCO₃ produced were highly pure, these value-added products could eventually reduce the overall cost of the carbon sequestration process.

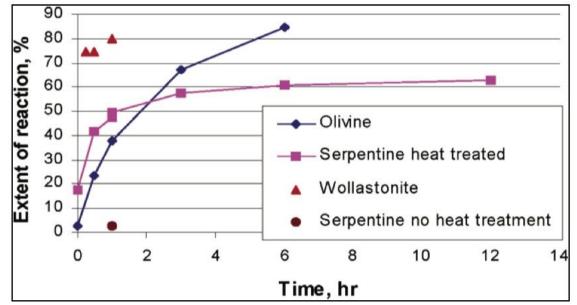
Gerdemann, et al, (2004, 2007) The U. S. Department of Energy's Albany Research Center is investigating mineral carbonation as a method of sequestering CO₂ from coal-firedpower plants. Magnesium-silicate minerals such as serpentine Mg₃Si₂O₅(OH)₄ and olivine (Mg₂SiO₄) react with CO₂ to produce magnesite (MgCO₃), and the calcium-silicate mineral, wollastonite (CaSiO₃), reacts to form calcite (CaCO₃). It is possible to carry out these reactions either *ex situ* (above ground in a traditional chemical processing plant) or *in situ* (storage underground and subsequent reaction with the host rock to trap CO₂ as carbonate minerals). For *ex situ* mineral carbonation to be economically attractive, the reaction must proceed quickly to near completion. The reaction rate is accelerated by raising the activity of CO₂ in solution, heat (but not too much), reducing the particle size, high-intensity grinding to disrupt the crystal structure, and, in the case of serpentine, heat-treatment to remove the **chemically bound water.** All these carry energy/economic penalties. An economic study illustrates the impact of mineral availability and process parameters on the cost of *ex situ* carbon sequestration.

The carbonation rates are very dependent upon the **type of serpentine**. Mineral carbonation of antigorite and lizardite is very different; with antigorite $[(Mg, Fe^{2+})_3 (Si_2O_5)(OH)_4]$ having a carbonation efficiency of 92% and lizardite $[Mg_3(Si_2O_5)(OH)_4]$ of only 40% after thermo-activation.

In situ carbonation offers economic advantages over *ex situ* processes because no chemical plant is required. Knowledge gained from the *ex-situ* work was applied to long-term experiments designed to simulate *in situ* CO₂ storage conditions. The Columbia River Basalt Group (CRBG), a multi-layered basaltic lava formation, has potentially favorable mineralogy (up to 25% combined concentration of Ca, Fe^{2+} , and Mg cations) for storage of CO₂. However, more information about the interaction of CO₂ with aquifers and the host rock is needed.

The research included resource evaluation, kinetic studies, process development, and economic evaluation. An initial cost estimate of \sim \$69/ton of CO₂ sequestered was improved with process improvements to \sim \$54/ton. The scale of *ex situ* mineral carbonation operations, requiring \sim 55 000 tons of mineral to carbonate, the daily CO₂ emissions from a 1-GW, coal-fired power plant, may make such operations impractical.

The following diagram compares olivine to serpentine dissolution at 185°C and 150 atm CO_2 in NaCl NaHCO₃ solution.



Teir, S. et al (2007) In this study, the dissolution of natural serpentinite in respective solutions of acids, bases and ammonium salts was investigated. Experiments performed at room temperature showed that H_2SO_4 was most efficient at extracting magnesium from serpentinite, followed by HCl, HNO₃, HCOOH and CH₃COOH. Experiments for determining the dissolution kinetics was performed at temperatures of 30, 50 and 70 °C in 2 M solutions of H₂SO₄, HCl and HNO₃. At 70 °C temperatures all magnesium was extracted from serpentinite in each of the three acid solutions tested during 1–2 h. Also, a large part of iron in serpentinite was extracted, while very little silicon dissolved (<4%). The dissolution rate seemed to be limited by

product layer diffusion for serpentinite particles with a size distribution of 74–125 μ m. The apparent activation energies were 68 kJ/mol for dissolution in H₂SO4, 70 kJ/mol for dissolution in HCl, and 74 kJ/mol for dissolution in HNO₃.

Although the experiments show that common mineral acids can extract magnesium from serpentinite in time frames relevant for industrial processes, a successful carbonation process must also manage to precipitate magnesium carbonate and recycle most of the additional chemicals used. Therefore, more research on process development is needed before serpentinites can be used for long-term storage of CO₂.

Alexander, G. et al (2007) In this work, a statistical design of experiments was conducted to ascertain the effect of acid concentration, particle size, and reaction time and temperature on the leaching of magnesium from serpentine using sulfuric acid. Results demonstrated that acid concentration provided primary control on the dissolution via the removal of water, which is closely correlated with the extraction of magnesium from serpentine. Particle comminution to a median size less than 163 μ m remained an important consideration in increasing reactivity and liberating magnetite. Single variable experimentation demonstrated dissolution of 46% and 70%, over a baseline test, occurred for increased reaction time and temperature, respectively.

Brent, G.F. and Petrie, J.G. (2008) This study focused on using the techniques developed by ARC for the *ex-situ* sequestering of CO₂ captured from coal fired power plants, instead of injecting it underground. This work focused on serpentine as it is far more abundant and widespread in Australia than olivine and wollastonite.

The process uses aqueous buffer solutions of NaCl and NaHCO slurred with **ground serpentine**. The role of the buffers is to simultaneously maximize serpentine dissolution and magnesium carbonation rates. Carbonation is achieved via contact with supercritical CO₂ at reaction conditions of 115 atm and 155°C. The final conclusion of the ARC team was that **serpentine required thermal or intense mechanical pre-treatment for activation (essentially a dehydroxylation step), and that this introduced prohibitive energy and cost penalties, effectively ruling out a viable serpentine process.** However, the ARC report did not consider pre-treatment via direct thermal activation in a fuel-fired furnace, nor **did it include any heat recovery from the exothermic carbonation reaction**, both of which offer significant reductions in net processing costs.

Other routes to process improvements have also been identified, including energy integration, improved carbonation reactor design, and more effective solids separation recycle technologies. These routes are under investigation in current research programs. Whilst not wanting to understate the technical challenges inherent in such new process development, **initial results are encouraging and indicate that a substantial reduction in the ARC-quoted energy penalty and costs may be achievable.**

The key to improving the overall viability of the ARC process is to consider means by which the net energy requirement for the process can be reduced. The process envisaged here focusses on sequestration of emissions from coal-fired power generation for regions where viable geosequestration or other options do not exist.

The amount of serpentine ore required would equate to less than half the amount of material currently mined in Hunter Valley open cut mines for each ton of coal processed.

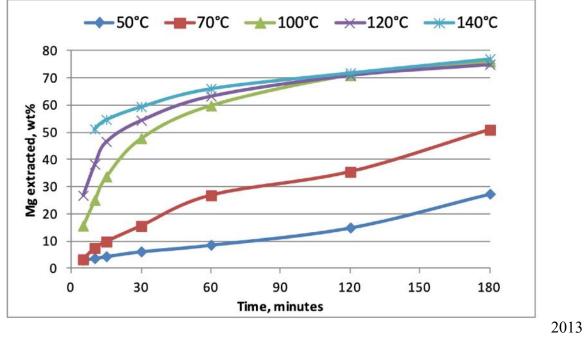
Fortuitously, the largest occurrence of serpentinite minerals in Australia lies in the so-called **Great Serpentinite Belt** (see for example McEvilly et al. 2004) of the Peel Fault system, stretching for well over 100 km from Tamworth.

The total current CO₂ emissions from NSW power stations are around 60 Mt pa. Four large facilities in the Hunter region make up over 70% of these emissions (Saddler et al., 2004). A future scenario can be envisaged where two to four new power generation plants, producing an equivalent 60 Mt CO₂ pa from about 25 Mt coal pa, are centered on a serpentine mining industry still in reasonable proximity to the Hunter Valley or Gunnedah coalfields. The magnitude of a serpentine mining industry required to sequester all these emissions would be about 180 Mt pa. This may require 10 medium scale open pit serpentine mines each producing 15 - 20 Mt pa.

Krevor and Lackner, (2011) Neutral organic salts such as sodium oxalate, and citrate enhance dissolution kinetics of serpentine in the circum-neutral pH range appropriate for mineral carbonate precipitation and have potential for use in an enhanced carbonation process. Concentration and temperature dependencies for the dissolution of antigorite serpentine in the presence of the citrate ion are experimentally derived under weakly acidic conditions. Rates are shown to be several orders of magnitude higher in the presence of citrate than in the weakly acidic solution alone.

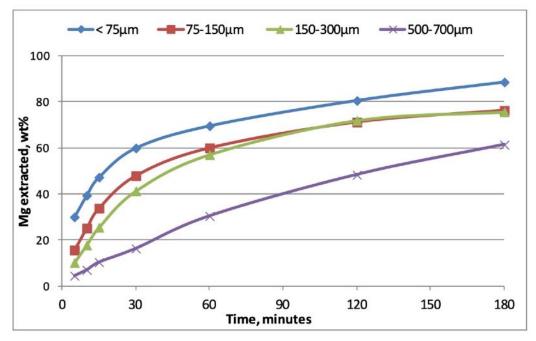
Orlando, et al (2011) In order to perform geological sequestration of CO₂, **serpentinite** should be dissolved by acids or by aqueous solutions. At atmospheric pressure serpentinite is efficaciously dissolved at 70 °C using **acid attacks**. At higher P-T conditions, significant carbonation occurs at 30 MPa (megapascal) and 300 °C using CO₂ saturated aqueous solutions.

Sanna, A. et al (2013). The extraction of Mg from lizardite serpentine was studied as a function of temperature, particle size, of NH₄HSO₄ concentration and other variables. Some of these results are shown below.



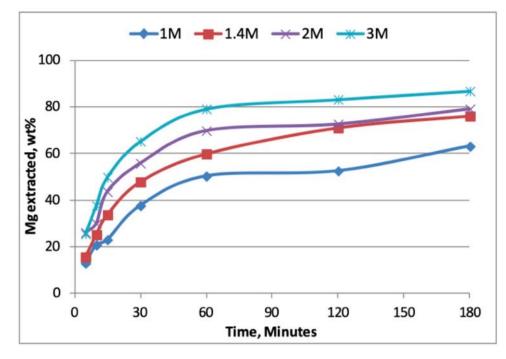
Effect of temperature and time on Mg extraction from serpentinized lherzolite

The clustering shows that once the temperature of 100°C is reached, after 60 minutes, relatively less additional extraction of Mg was noted.



Effect of **particle size** and time on Mg extraction from serpentine (100°C, 50 g/l, 1.4 M NH₄HSO₄, 800 rpm).

As shown in many studies, the smaller the particle size the more efficient the dissolution. 75 um is still a fairly large particle size. Although temperature and salts were also involved, these results suggest that grinding to < 5 um size may not be necessary for EW on soils.



Effect of NH₄HSO₄ concentration and time on Mg extraction from serpentine.

Sanna, A. et al (2014) reviewed the literature relevant to the use serpentines.

Daval et al (2013a) reported that a critical factor in the weathering of serpentine is the common formation of amorphous Si-rich surface layers (ASSLs), which may hinder contact between the fluid and the mineral surface. By considering ASSL as a separate phase that can control silicate dissolution rates, extrapolated laboratory-based rates at conditions relevant to the field can be lowered by up to several orders of magnitude, thereby decreasing the large gap between laboratory and natural rates. This has important implications for more accurately modeling chemical weathering reactions, so important today for the C cycle and CO_2 sequestration. In their studies samples were in the size range of 300–500 um.

Daval et al (2013b) examined the role of pH (2.5 to 6.7), temperature (27 to 90°C and pCO₂. For any single pH–T condition **lizardite dissolution** rates were **orders of magnitude lower than those of anhydrous basic silicates, such as olivine or pyroxenes**. The sluggishness of the dissolution reaction probably explains the slow carbonation rates that have been measured in previous studies. Lizardite, Mg₃Si₂O₅(OH)₄, volumetrically is the most common serpentine species.

Shikazono, N.et al. (2014) Dissolution experiments were performed on serpentinite samples containing serpentine, brucite, olivine and pyroxene from Mt. Iwanai, Hokkaido.

From the results, we obtained dissolution rate constants for serpentine $(Mg,Fe)(Si_2O_5)(OH_4)$, brucite $(Mg(OH)_2)$ and olivine $(Mg,Fe)_2SiO_4)$ as functions of pH.

The results indicate that the amounts of primary minerals (brucite, olivine, and pyroxene) **decrease over time due to dissolution**. Artinite $(Mg_2(CO_3)(OH)_2 \cdot 3H_2O)$ forms as a product of this dissolution in the early stages and then its amount decreases as magnesite (MgCO₃) forms. 100% of the injected CO₂ will be fixed as magnesite in 22 years for sample A, a harzburgite serpentinite, and in 3 years for sample B, a dunite serpentinite. These periods are very short compared with other types of rocks like basalt, granite, and sedimentary rocks from Japan studied in our laboratory. This indicates that the serpentinite rocks are potentially useful aquifer host rocks for underground sequestration of CO₂.

Swanson, E. J. (2014) Accelerated weathering of ultramafic rocks is an environmentally benign route to a thermodynamically and kinetically stable form of carbon. However, the reactions are relatively slow and achieving the reaction rates necessary to justify incorporation into an energy conversion system is challenging. Comparing the freshly ground olivine cases with the literature's values, it is evident that the particle size, particularly smaller than 20 μ m, is significantly involved in mineral dissolution and carbonation.

One conclusion was that even without the pretreatments, some of the Mg-bearing minerals showed promising results for carbon storage. However, the conversion of magnesium serpentine $[Mg_5(CO_3)_4(OH)_2:4H_2O]$ to anhydrous magnesium carbonate $[MgCO_3]$ is a challenging reaction to achieve reliably and reproducibly at reasonable process conditions. The persistence of metastable magnesium carbonate species reduces the overall efficiency of a carbon mineralization process due to the bulky nature and solubility limitations of the hydrated magnesium carbonates. In this study it was shown that the presence of magnesite seeds avoided the formation of metastable species entirely. It was also shown that it is possible to grow magnesite crystals below 100 °C and with low CO₂ partial pressures, something that was previously thought far more difficult.

Werner, M.S. (2014) The challenge of using serpentine to sequester CO₂ is tackled by carbonating the magnesium silicate serpentine, the world's most abundant mineralization precursor that can be thermally activated for enhanced reactivity, in an aqueous medium at low CO₂ pressures. Key to success for any aqueous mineralization process is to understand how to overcome the slow dissolution kinetics of the mineralization precursor.

The results suggested that the reaction progress was hindered by a **passivating layer of re-precipitated silica, quartz, or carbonates**, as well as by equilibrium limitations. Various strategies to improve the carbonation efficiency were tested. The logical next step in process development was to explore the carbonation potential of the activated serpentine at flue gas conditions.

The batches of Ca- and Mg-silicates used were subjected to mechanical pretreatment by **attrition grinding**, to maximize the specific surface of the minerals, i.e., the surface per unit mass available for Mg/Ca-extraction. **Attrition grinding** is a process in which the rock is ground over a sieve. Particles that a small enough to pass through the sieve are removed and only unground rocks remain. With time they are also ground up and pass through the sieve, i.e. by attrition.

The hydrated Mg-silicate serpentine was **thermally activated**, which creates an even higher specific surface area and destabilizes the crystal lattice, thus making the mineral more susceptible to dissolution.

Chemical additives were used to increase the ionic strength and the alkalinity of the solution. Obviously, any additive would have to be fully recoverable in a real process. While the single-step ARC process can be viewed as a benchmark, research has ever since striven after further improvements of the technology at affordable cost. Double-step and multi-step process designs were developed that allow for changing the operating conditions between the different stages, to promote extraction and precipitation separately.

To avoid the cost associated to a preliminary capture step, the most recently proposed routes aim at capturing the CO_2 from a **flue gas** at the same time while mineralizing it. Many of these studies relate to the utilization of flue gas. This is the gas that emanates from coal fired power plants.

The following table is an overview of the most important CO₂ mineralization techniques.

Proces s		Suitable solid feed	Operating $T [^{\circ}C]$	$\begin{array}{c} \text{Operating} \\ p\text{CO}_2 \ [\text{bar}] \end{array}$	Additives
Single step aqueous carbonation	ARC benchmark	wollastonite, silicious waste materials	>100	>15	optional (NaHCO ₃ : NaCl)
		olivine, HT serpentine and mine tailings	>150	>80	optional (NaHCO ₃ , NaCl)
2		CaO-rich waste materials	<100	<3	none
Double step aqueous carbonation	pH-swing	any	various	various	strong base, strong acid
		any	<100	<1	$\rm NH_4SO_4$
	pH-buffer	wollastonite, waste materials	various	$p{\rm CO}_2\text{-swing}$	pH buffer agents
	T - p CO $_2$ -swing	HT serpentine, waste materials, wollastonite	T-swing	$p{\rm CO}_2$ -swing	none
Aqueous carbonation using ligands		olivine, serpentine	<120	various	chelating agents
ÅA process (3-step)	NH ₃ - driven precipita- tion	serpentine	400, 20, 500	20	$\rm NH_4SO_4$
Alkaline solution based	manufactured alkalinity	brines, red mud	low to moder- ate	low to moderate	alkalinity (NaOH)
Single step dry carbonation		CaO-rich waste materials (APC-residues, fresh concrete)	25-500	various	none

Du Breuil, et al (2019). Serpentine minerals $(Mg_3Si_2O_5(OH)_4)$ have shown great potential for carbonation. A way to improve yield is to thermally activate serpentine minerals prior to the carbonation reaction. This step is of great importance as it controls Mg^{2+} leaching, one of the carbonation reaction limiting factors. Previous studies have focused on the optimization of the thermal activation by determining the ideal activation temperature. However, to date, none of these studies have considered the impacts of the thermal activation on the efficiency of the aqueous-phase mineral carbonation at ambient temperature and moderate pressure in flue gas conditions. Several residence times and temperatures of activation have been tested to evaluate their impact on serpentine dissolution in conditions similar to mineral carbonation. A novel approach to quantify the meta-serpentine formed during dehydroxylation is introduced. The most suitable mineral assemblage for carbonation is found to be a mixture of the different amorphous phases identified. This study highlights the importance of the mineralogical assemblage obtained during the dehydroxylation process and its impact on the magnesium availability during dissolution in the carbonation reaction.

Thermally produced amorphous phases enhance Mg²⁺ solubility during carbonation reaction. Furthermore, the formation of meta-serpentine, resulting in a complete dehydroxylation, significantly upgrades Mg²⁺ leaching yield.

Haque, F. et al. (2019) Candidate materials for enhanced weathering olivine, pyroxene, and serpentine, given their reactivity with CO₂ and global availability. When these finely crushed silicate rocks are applied to the soil, the alkaline earth metal cations released during mineral weathering gradually react with carbonate anions and results in the formation of pedogenic carbonates which, over time, and under the right conditions, can accumulate in the soil. The CO₂ sequestration potential via alkaline mineral soil amendment is quantified and shows that it has the potential to serve as a climate change stabilization wedge. <u>The important aspect of this report is the conclusion that the only pretreatment required is finely grinding the respective rocks.</u>

Tebbiche, I. et al (2021) In this paper, **heat integration was coupled with serpentine preheating temperature** optimization. This was the first time applied to a mineral carbonation process. For this, a process was selected with **the aim to minimize its heat demand**. Aspen® Energy Analyzer software was used for heat integration with pinch analysis. The mineral carbonation plant considered here **processes 100 tons of serpentine per hour**, with Mg content of 237 kg per ton of rock, corresponding to 0.88 million tons per year to treat 0.5 million tons of CO₂ emitted from a cement plant. In the base case considered for heat integration, 50% of the serpentine magnesium content was converted to hydromagnesite using 30% of the flue gas CO₂ which means that **5.85 tons of rocks were required to capture 1 ton of CO₂**.

The serpentine **preheating temperature** was optimized as 400 °C. Application of heat integration at this solid preheat temperature reduced the process heat demand by 25% compared to our previous study, as 5.0 GJ per ton of CO_2 captured or 9.5 GJ per ton of CO_2 avoided. This corresponds to 0.86 GJ per ton of ore as the process heat demand was only attributed to the mineral activation. Furthermore, the uncertainty behind unknown parameters such as activated serpentine heat capacity and solid heat transfer coefficient was evaluated to validate the study.

IV. Serpentine Dissolution: Field Studies on Cropland or Simulated Field Studies

Baumeister (2012) The author's studies were for a master's thesis and was entitled **Chemical Weathering of the Mafic Minerals Serpentine and Olivine in Natural Environments.** This covers the information relevant to what we are seeking, i.e., what is the natural weathering rate of serpentine compared to olivine.

Significant amounts of carbon dioxide are consumed during the natural weathering process, or dissolution, of the mafic minerals, olivine, and serpentine. There have been many studies of the rate of olivine in the laboratory (see references in the thesis). By contrast, serpentine dissolution studies performed at temperatures and pH ranges relevant to the natural environment are very limited.

A serpentine dissolution rate was measured in a natural setting using catchment hydrochemical data which was orders of magnitude slower than published laboratory rates. Most studies of serpentine in a natural setting have focused on soil and secondary mineral formation (see thesis for references).

The authors studied the characteristics of serpentinite weathering from the unweathered parent rock to the soil surface at two sites in the Klamath Mountains of northern California. Samples of both soils and rock cores from each study site tested positive for iron-oxidizing bacteria, and signs of oxidized iron were observed on weathering rinds in the soil and rock cores. In the weathered samples, mineral dissolution appears to follow a specific order (from first to dissolve to most resistant): pyroxene > iron-rich serpentine > magnesium-rich serpentine > aluminum-rich serpentine. This mineral order is likely based on mineral dissolution kinetics, possible effects of biological iron-oxidation, and cation substitutions that can act to stabilize the mineral structure.

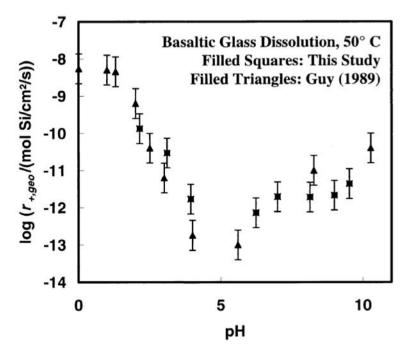
In addition to the Klamath sites, the authors also examined the dissolution of olivine in a natural environment at Black Rock Flow, in central Nevada. These findings help quantify the incipient processes affecting serpentine soil formation and provide the first known dissolution rate for naturally weathered olivine in an arid environment. The forsterite dissolution rate measured from etch pits, after adjusting for roughness, is 3.48×10^{-15} mol/m²/s, which is approximately four to five orders of magnitude slower than published laboratory dissolution rates at a pH of ~7-9.

Power, et al. (2020) The authors studied CO₂ mineralization at the Baptiste deposit which is located within the Decar nickel district in British Columbia, Canada and was a promising candidate for a CO₂ sequestration demonstration project. The deposit contains awaruite (nickel-iron alloy) hosted in an ultramafic complex, which is dominated by serpentine [Mg₃ Si₂O₅(OH)₄ ~80 wt.% and contains reactive brucite, Mg(OH)₂ 0.6–12.6 wt.%. Experiments were conducted with the aim of determining the potential for this deposit to sequester CO₂ via direct air capture of atmospheric CO₂ and carbonation using CO₂-rich gas. The experimental direct capture rate was 3.5 kg CO₂/m/yr and would sequester 17 kt CO₂/yr based on year-round reaction and when extrapolated to the scale of the proposed tailings facility (5 km²). This rate can be increased by ~5 times (19 kg CO₂/m/yr) when aerating the tailings and would offset CO₂ emissions by 95 kt CO₂/yr which is 19–25% offset of projected CO₂ emissions.

While the ore was described as fine grained no data on particle size was given.

V. Basalt Dissolution: Laboratory Studies

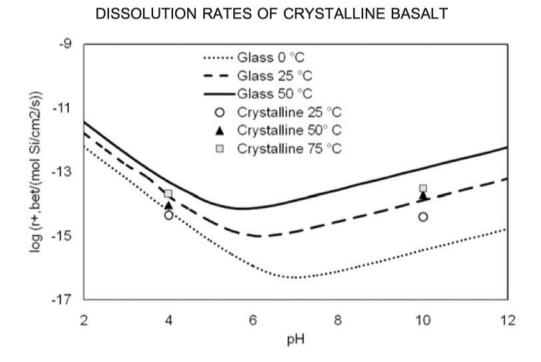
Gislason and Oelkers (2003) examined the dissolution rates of basaltic glass at 50°C and showed and inverted curve with the lowest rates of 10⁻¹³ mol Si/cm²/s at pH 5.



Variation of measured geometric surface area normalized basaltic glass dissolution rates at 50°C as a function of pH.

Golubev et al (2005) also examined the dissolution rates of basaltic glass at 50°C at various pHs and obtained an inverted curve with it lowest rate at pH 6. Their curve is presented above in the diagram shown by Snæbjörnsdóttir et al (2020).

Gudbrandsson, S et al. (2008) examined basalts from a dyke on Stapafell Mountain on Reykjanes peninsula in Iceland because of its similarity with previous experiments on dissolution rates on basaltic glass by Oelkers and Gislason (2001) and Gislason and Oelkers (2003).



Dissolution rates of crystalline basalt (symbols) are compared to modelled dissolution rates (curves) of basaltic glass from the same location (Gislason and Oelkers, 2003).

Comparison of dissolution rates of basaltic glass and of crystalline basalt of similar chemical composition (from Gislason and Oelkers, 2003) indicates slightly lower rates for crystalline material.

These three studies indicate that the unique inverted curve for dissolution rates of basalt by pH is reproducible.

Vienne, A. et al (2022) investigated enhanced weathering in a mesocosm experiment with *Solanum tuberosum* (Irish potato) growing on alkaline soil. The addition of 50 t basalt/ha significantly increased alkalinity in soil pore water and in the leachate losses, indicating significant basalt weathering. The duration of the experiment was 99 days. Soil and pore water nickel increased upon basalt addition, but nickel levels remained below regulatory environmental quality standards. The basalt amendment significantly decreased nitrogen leaching, indicating the potential for EW to provide benefits for agriculture and for the environment. Applying 50 t of basalt per ha corresponds with a theoretical maximum of 20.8 and 11.2 t CO₂/ha through enhanced weathering and mineral carbonation respectively. It may take several decades for this to be reached. They recognized that applying several tens of tons of basalt/ha in practice would result in substantial transportation costs and that this application rate is higher than for conventional fertilizers.

VI. Basalt Dissolution: Field Studies on Cropland or Simulated Field Studies

Edwards....Beerling, et al (2017) reviewed the many advantages of using EW on croplands in the tropics, including the fact the weathering occurs significantly faster in the moist, humid tropical areas (see hot spots).They recommended using **crushed basalt with its lower risk of releasing toxic heavy metals.** Additional benefits included decreasing soil acidification and increasing phosphorus supply, both known to promote higher crop yields. The noted the potential pitfalls include the impacts of mining operations on deforestation, the energy required to crush and transport silicates. The note, as we have, that the energy costs of mining, grinding and transportation will **be mitigated with the increasing use of solar and other carbon-free sources.**

Kelland et al. (2020) Land-based enhanced rock weathering (ERW) is a biogeochemical carbon dioxide removal (CDR) strategy aiming to accelerate natural geological processes of carbon sequestration through application of crushed silicate rocks, such as basalt, to croplands and forested landscapes. However, the efficacy of the approach when undertaken with basalt, and its potential co-benefits for agriculture, require experimental and field evaluation. Here they report that amending a UK clay-loam agricultural soil with a high loading (10 kg/m^2) of relatively coarse-grained crushed basalt significantly increased the yield $(21 \pm$ 9.4%, SE) of the important C4 cereal Sorghum bicolor under controlled environmental conditions, without accumulation of potentially toxic trace elements in the seeds. Yield increases resulted from the basalt treatment after 120 days without P- and K-fertilizer addition. Shoot silicon concentrations also increased significantly $(26 \pm 5.4\%, SE)$, with potential benefits for crop resistance to biotic and abiotic stress. Elemental budgets indicate substantial release of base cations important for inorganic carbon removal and their accumulation mainly in the soil exchangeable pools. Geochemical reactive transport modelling, constrained by elemental budgets, indicated CO₂ sequestration rates of 2-4 t CO₂ /ha, 1-5 years after a single application of basaltic rock dust, including via newly formed soil carbonate minerals whose long-term fate requires assessment through field trials. This represents an approximately fourfold increase in carbon capture compared to control plant-soil systems without basalt. Our results build support for ERW deployment as a CDR technique compatible with spreading basalt powder on acidic loamy soils common across millions of hectares of western European and North American agriculture.

Rinder, T. and von Hagke, C. (2021) reviewed the state of research for enhanced weathering of basalt. A < 10 μ m grain size could remove $\approx 2\%$ of Austria's greenhouse gas emissions per year. For larger grain sizes, transport emissions become important. Field weathering rates reduce the sequestration potential estimated in previous studies. Uncertainties related to actual CO₂ drawdown under field conditions are still large.

This article reviews of the current state of research and estimates the CO₂ drawdown for scenarios using basalt powders of different particle size distribution (<100 μ m, <10 μ m and <1 μ m). Calculated with a modified shrinking core model, the amount of powder dissolved within a timeframe of 10 years is approximately 16% (<100 μ m), 55% (<10 μ m) and 99.9% (<1 μ m). This corresponds to a gross CO₂ removal of 0.045 t CO₂/ t for <100 μ m particle size, and 0.153 t CO₂/ t of <10 μ m rock. Our estimates suggest that enhanced weathering will only significantly contribute to net CO₂ drawdown if grain sizes (<10 μ m) are used. Under these conditions the large-scale application of particles with a diameter <10 μ m may remove about 2% of Austria's annual Greenhouse gas emissions.

They discuss challenges towards this goal, including the enormous amounts of rock needed and the energy requirement related to grinding, as well as uncertainties related to actual field weathering rates. Those uncertainties hinder the precise quantification of CO_2 drawdown as of now. While enhanced weathering remains a promising path for climate change mitigation, further research at laboratory and field scale is required to put this technology to optimal use.

Houlton, (2021) Dr. Benjamin Houlton of the Global Environmental Studies, John Muir Institute of the Environment, at the University of California, Davis, has examined the effect of mafic rocks on a 50-acre test plot in California. The results had not been published but were described in an Energypost.eu July 24, 2021, article entitled *Enhanced Weathering: Crushed Rocks Spread on Farmland can Capture Billions of Tons of CO2/year.*

Houlton stated that "At the Working Lands Innovation Center, we are conducting **perhaps the largest enhanced weathering demonstration experiment on real farms in the world.** We are partnering with farmers, ranchers, government, the mining industry, and Native American tribes in California on some 50 acres of cropland soil amendment trials. We are testing the effects of rock dust and compost amendments on greenhouse gas emissions from the soil, carbon capture, crop yields, and plant and microbial health. Our initial results suggest that **adding basalt and wollastonite**, **a calcium silicate mineral**, **increased corn yields by 12% in the first year**."

"Nations need a portfolio of solutions to create negative emissions. Enhanced weathering is poised for rapid scale-up, taking advantage of farm equipment that is already in place, global mining operations and supply chains that currently deliver fertilizers and seeds worldwide. By addressing soil erosion and food security along with climate change, I believe rock weathering can help humans escape the hard place we find ourselves in today."

Buckingham et al (2022) published a study entitled *Soil core study indicates limited CO*₂ *removal by enhanced weathering in dry croplands in the UK*. In this study crushed basalt was applied to a UK agricultural soil in a 14-month soil core study. They concluded that five years of basalt application over UK cropland could remove 1.3 ± 0.1 MtCO₂ yr. This rate of removal of CO₂ was considerably slower than model predictions. These low rates were due in part to low water flux in dry UK cropland.

The study was carried out using soil cores removed from UK cropland. Cores were exposed to natural weather conditions throughout a 14-month time series and soil solution was sampled in 10–20 cm intervals in the core to provide insight into the fate of dissolution products with soil depth. The study assessed the rate and chemistry of basalt dissolution 8 months after addition at a high application rate of 100 t basalt/ha. They concluded that in lime rich, unirrigated UK soils this treatment released alkalinity at a rate of 310 ± 30 eq/ha/yr and could remove $10.2 \pm 0.8 \text{ kg CO}_{2/}$ ha/yr. Soils release CO₂ and this rate only removed 3% of current UK agricultural CO₂ emissions. This is 5- to 25- fold slower than previous modelled assessments, likely due to complexities of soil systems and to water limitation on alkalinity release. Two caveats of this study are that the particle size of the crushed basalt was 125 to 250 microns, significantly larger than the recommended size of 1 micron for a maximum rate of weathering, and that basalt weathers at a rate of several orders of magnitude slower than olivine.

VII. Wollastonite Dissolution: Field Studies on Cropland or Simulated Field Studies

Hague, et al (2020a) Wollastonite (CaSiO₃) has been commercialized in Ontario as an agricultural soil amendment for several years, but it is not known if or how much CO₂ is sequestered annually. In this present study, wollastonite-amended soils were collected from three commercial-scale fields located in Ontario: a leafy vegetables farm in the town of Paris (Field 1); a potato farm in the settlement of Alliston (Field 2); and a soybean farm in the city of Woodstock (Field 3). The **soil inorganic carbon (SIC)** content was higher in all soils that had been amended with wollastonite, compared to controls, and in **Field 1 the SIC content was 2.6 times higher in soil amended thrice with wollastonite compared to a single application**. This work provides further evidence, here for the first time at a regional scale, **that soil amendment with alkaline silicates can be an effective geoengineering tool for climate change mitigation**.

Haque et al (2020b) The first objective of this study was to evaluate the effect of mixing a wide range of dosages of wollastonite, as a soil amendment, on the growth performance of two leguminous plants frequently used in agricultural sector: soybean and alfalfa. The plants were grown with different wollastonite dosages (3-20 kg·m⁻² for soybean and 3-40 $kg \cdot m^{-2}$ for alfalfa), for a duration of 14 weeks in a microplot experiment in Ontario, Canada. The second objective was to find evidence of enhanced weathering of wollastonite in soil, in addition to the augmentation of inorganic carbon content in soil. Wollastonite increased the soybean yield by two-fold in the plot amended with 10 kg \cdot m⁻². At all dosages, wollastonite increased the alfalfa growth in terms of height and above-ground biomass dry weight, as well as root biomass. The rate of CO₂ sequestration, at optimum wollastonite dosage, reached 0.08 kg CO₂/m²/month. XRD and SEM-EDS analyses indicated accumulation of calcite in wollastonite-amended soil and formation of other weathering products. The results obtained from this study help to understand the impact of wollastonite soil amendment on agronomy and will aid in implementing such negative emissions technology by informing farmers and industry alike that the use of wollastonite contributes toward global climate change mitigation while supporting crop yield. The findings of this study add to the existing body of knowledge on enhanced weathering as an atmospheric CO₂ removal technology, providing further evidence that wollastonite weathering in agricultural soils can lead to significant capacity for CO_2 sequestration as inorganic carbon, while concurrently promoting plant growth.

VIII. Concurrent Grinding

Concurrent grinding refers to incorporating low energy, attrition-type grinding during the reaction of serpentine rocks with heat, acid or other chemical or physical treatments. Since several studies have shown that it is a very efficient method of dissolution of serpentine. There are two aspects to the development of this technique. The first is the use of strong acid (< 1M) to the dissolution of serpentine. The second was the use of concurrent grinding while in the presence of the acid.

Klaus Lackner et al (1995) were the first to propose carbon dioxide sequestration by the dissolution of serpentine in strong acid. They found that the thermodynamics for both the dissolution of serpentine and the formation of carbonates were favorable.

Albany Research Center the Lackner paper led to many studies of the potential role of the carbonation of several minerals. As reviewed above, O'Connor and his team at the Albany Research Center conducted several studies on CO₂ at high pressure for the direct carbonation of serpentine. It was found, however, that **pre-treatments such as roasting the serpentine at high temperature and/or grinding to a fine size, were necessary**. These treatments resulted in an amorphous structure of the serpentine. This removed the highly ordered structure of serpentine allowing different reagents to interact with the interior metals. The problem with these treatments was that they were very expensive. The level of this expense slowed enthusiasm for these techniques, work continued.

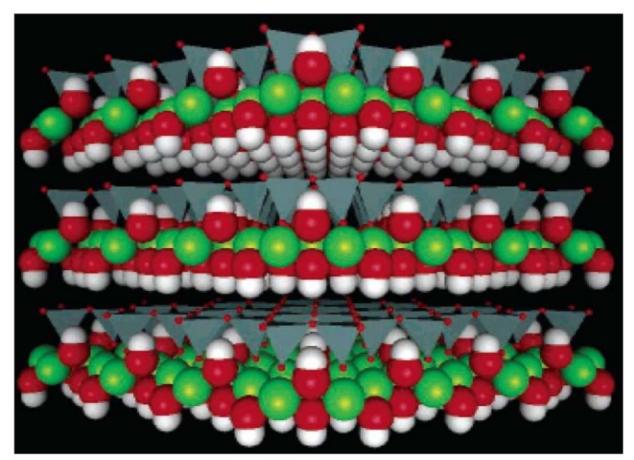
A potential solution of splitting the chemistry into two steps: a chemical extraction of magnesium at low pH and carbon dioxide adsorption at high pH. was proposed by Park et al (2003, 2004). She and her colleagues showed that use of both a mixed acid/organo-ligand solution and internal *in situ* grinding enhanced dissolution. They found that by slowly increasing the pH of the solution, impurities could be precipitated out, and then by addition of carbon dioxide at atmospheric pressures and temperatures, magnesium carbonate would form. It was also demonstrated that the kinetics of **the extraction of magnesium from serpentine could** be at **least doubled by the incorporation of a low energy, attrition-type grinding during the dissolution, i.e., concurrent grinding.**

Previous studies demonstrated that a silica diffusion barrier forms on the surface of serpentine particles as dissolution occurs and that this can effectively slow or even stop the digestion kinetics of serpentine in acid. The concurrent grinding solves this problem. That grinding is done by fluidizing silica beads with the reaction slurry of acid and mineral particles. The apparent advantage is rapid refreshment of the surface at energy levels that are expected to be consistent with a fluidized-bed reactor or a rapidly agitated continuously stirred tank reactor (Park and Fan, 2004). A drawback was that the fluidization was done in a complex system of expensive chemicals. In addition, kinetics of the system was not provided, thus limiting comparisons to other proposed methods.

Tier, et al, (2007) (see also above) found that sulfuric acid extracted the most magnesium from serpentine in the shortest time and that the extraction yield did not increase past two molar concentrations for sulfuric acid and examined kinetics.

Van Essendelft, (2008, 2009a,b, 2010) examined the kinetics of concurrent grinding in acid. Serpentine is a highly ordered ultramafic magnesium silicate structure consisting of alternating sheets of brucite-like material and silica-like material. This highly ordered structure causes the formation of a silica barrier around the mineral particles that can slow or even stop the kinetics as the particles dissolve. The physical behavior of this layer causes a shift in kinetic behavior from surface limited kinetics to diffusion limited kinetics. However, it has been shown that both behaviors are important at the same time and vary by particle size. Further, it has been shown that the kinetics can be greatly accelerated by incorporating concurrent, low energy, attrition-type grinding during the chemical reaction. It was found that particle shape as well as size plays a critical role in the kinetics.

The following diagram shows the three-dimensional structure of serpentine.



The Ideal Structure for Serpentine (McKelvy, et al (2004) The grey tetrahedrons with red tipped ends are silica groups, the large green spheres are magnesium, and the red and white conjoined spheres are hydroxides. It is a very ordered structure with silica groups bound together in their basal plane and a brucitelike sheet sharing the electro-negativity of the antipodal oxygen of the silica.

There were three important results from this study. First, **simultaneous acid etching and grinding with a single strong acid significantly increase the overall reaction rate and yield**. The author felt that an extraction of such high conversion in such short time with this type of serpentine without solids modification or pretreatment has not previously been reported in the literature. Second, the acid etching prefers grain boundaries and defects, as is expected. This suggests that a focus on comminution techniques that can impart high amounts of structural defects could be helpful. Third, and most importantly, grinding is not sufficient to keep surfaces refreshed under the current conditions. That is, the initial stages of digestion proceed quickly and appear to be surface reaction limited, while the later stages appear to be diffusion limited. Using a modified shrinking core model with a hypothetical spherical particle size distribution (PSD), the effect of grinding appears to change the effective diffusivity of the gel layer surrounding the un-reacted core.

In conclusion, it was demonstrated that the combination of physical and chemical methods can lead to greatly increased kinetics. Further, it has been shown that simple strong acids can be used to greater effect than mixtures of acid and organic agents.

Rashid et al, (2019) Vast reserves of **peridotite** and **serpentinite** rocks can be utilized for the safe and permanent sequestration of global CO₂ emissions via aqueous mineral carbonation. These, and indeed most feedstocks used in mineral carbonation **require ultrafine** grinding and/or heat-activation, to engender significantly enhanced reactivity in the rock such that it can then be carbonated. Both activation processes are energy intensive and present significant obstacles to the commercial application of mineral carbonation. Here they show that these limitations can be addressed, at least in part, through the application of a concurrent or in operando grinding technique which does not require feedstocks which have been subjected to prior ultrafine grinding nor heat-activation.

Concurrent (in operando) grinding experiments. the **dunite slurry** was charged into the reactor liner, along with grinding media. The reactor was assembled and **heated** to the desired temperature. The reactor was then pressurized with CO_2 to 65 or 130 bar and carbonation and grinding proceeded simultaneously for the desired time period.

Thus, unlike the previous studies where concurrent meant concurrent with strong acid, in the **Rashid et al studies concurrent meant along with grinding media, heat, and pressurized CO**₂.

Concurrent grinding is shown to result in a significant increase in magnesite yields for non-heat activated feedstock, prepared such that fines (<20 μ m particles) were excluded from the feed. They assert that concurrent grinding may be a suitable technique for the processing of feedstocks such as those containing significant proportions of **forsterite and pyroxene**, minerals which are unresponsive to thermal activation for use in aqueous mineral carbonation. This study also investigates the effect of different grinding media particle size on reducing the PSD of the feed. Optimum ratio of grinding media size to feed particle size, optimum grinding media and slurry concentrations, optimum time for grinding and optimum impeller designs are determined for the system under study. The quantitative effect of grinding media concentration, slurry concentration, pressure and temperature on magnesite yield has been investigated.

For *in situ* grinding experiments, grinding and carbonation occur in separate steps. Concurrent (in operando) grinding during carbonation under the same conditions of pressure, temperature and solids loading resulted in higher final magnesite yields compared to *in situ* grinding experiments.

The authors concluded that concurrent grinding may be a suitable technique for the processing of feedstocks such as those containing significant proportions of forsterite and pyroxene, minerals which are unresponsive to thermal activation for use in aqueous mineral carbonation.

Rahsid, et al (2021)

- Concurrent grinding results six times higher magnesite yields.
- Concurrent grinding disintegrates silica-rich layers.
- Zirconia and stainless steel are better grinding media than alumina.
- Silica re-precipitation on grinding media was observed.
- Dunite is more reactive compared to olivine and lizardite.

Formation of silica-rich passivation layers formed on the periphery of reacting feed particles is one of the primary obstacles in obtaining high magnesite yields during direct aqueous mineral carbonation of peridotites and serpentinites. The disruption of the silica-rich layer around partially reacted grains as a result of concurrent grinding on the degree of carbonation (magnesite yield) was investigated in this work. Three types of naturally occurring magnesium silicate feedstocks, dunite, olivine and lizardite, as well as three types of grinding media, were examined.

Discrete size fractions of feed samples, with and without grinding media, were carbonated. SEM (scanning electron microscopy) readily disclosed the formation of a **silica-rich shell around a magnesium rich core** during carbonation. EDS (Energy Dispersive Spectroscopy) analysis was employed to study the elemental composition of reacted particles' shell and core. The method confirmed that **during concurrent grinding these silica rich layers were removed** and continuously produced a fresh surface available for further reaction. The **removal of the silica rich layer was shown to significantly improve magnesite yields up to a 600 % increase in yield**. Among the **three different grinding media used in this work**, **zirconia and stainless-steel media resulted in similar and highest magnesite yields**, which is believed to be due to a combination of their high densities and hardness.

The findings of this research showed that enhanced magnesite yields could be achieved for all feedstock without the need for energy intensive pre-treatment steps (e.g., ultrafine grinding and heat-activation). Moreover, concurrent grinding resulted in a magnesite yield when raw lizardite was carbonated.

IX. Olivine: The Potential Role of Electrolysis

Electrolysis plays a prominent role in OAE (see below). Does it also have a role to play in EW of cropland?

Zong-ging, (2007) describe a novel method for promoting carbon sequestration by mineral carbonation using electrolysis, which used the electrolytic reactor to electrolyze NaCl solution. The acid solution produced from anode was used to dissolve Mg^{2+} from serpentine, and the basic solution produced from cathode was used to adsorb CO₂ in simulation smoke, then these two solutions were mixed to form MgCO₃ deposition. The results indicate that the highest current efficiency could be when current was 0.5A. The acid solution produced from anode can dissolve Mg^{2+} . It was found that the deposition was mainly pure basic magnesium carbonate $[Mg_5(CO_3)_4(OH)_2.4H_2O]$, which was both environmentally benign and economical. The reactions can be processed at low pressure and relatively low temperature, and the pure H₂, Cl₂ and pure solid products can be obtained in this process, which makes the mineral carbonation process more economical.

Park, et al, (2015) This study proposes a method to fixate CaCO₃ stably by using relatively less energy than existing methods. After forming NaOH absorbent solution through electrolysis of NaCl in seawater, CaCO₃ was precipitated at room temperature and pressure. The analytical results showed that the CaCO₃ crystal product was high-purity calcite. The study shows a successful method for fixating CO₂ by reducing carbon dioxide released into the atmosphere while forming high-purity CaCO₃.

Kaczur et al, (2018) The recent development and market introduction of a new type of alkaline stable **imidazole-based anion exchange membrane** and related ionomers by Dioxide Materials is enabling the advancement of new and improved electrochemical processes which can operate at commercially viable operating voltages, current efficiencies, and current densities. These processes include the **electrochemical conversion of CO₂ to formic acid (HCOOH)**,

CO₂ to carbon monoxide (CO), and **alkaline water electrolysis, generating hydrogen** at high current densities at low voltages without the need for any precious metal electrocatalysts. The latter is an alkaline water electrolysis cell process, where the alkaline stable anion exchange membrane allows stable cell operation in 1 M KOH electrolyte solutions at current densities of 1 A/cm² at about 1.90 V. The cell has demonstrated operation for thousands of hours, showing a voltage increase in time of only 5 μ V/h. The alkaline electrolysis technology does not require any precious metal catalysts as compared to polymer electrolyte membrane (PEM) design water electrolyzer.

X. Serpentine: The Potential Role of Electrolysis

Li et al, 2009) described a new mineral carbonation process for CO_2 sequestration, using electrolysis of NaCl solution and serpentine as the source of Mg^{2+} to adsorb CO_2 in the simulating flue gas. It used the electrolysis of a NaCl solution to produce the HCl and NaOH. The HCl solution was used to dissolve Mg^{2+} from serpentine, and the NaOH solution was used to adsorb CO_2 in simulation smoke, then these two solutions were mixed to form MgCO₃ deposition at 358 K, which could be processed at relative low temperature and pressure, to further increase the solubility of Mg^{2+} from serpentine.

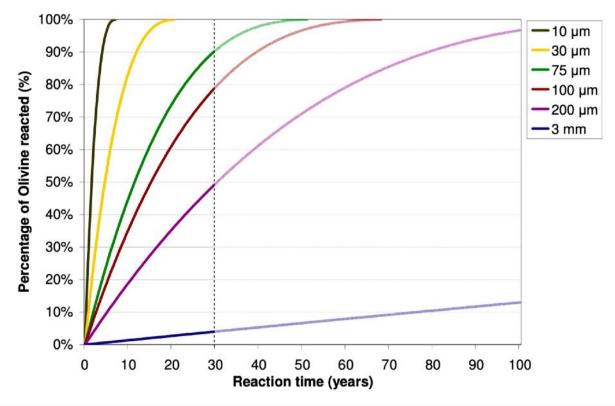
The heat pretreatment of serpentine under nitrogen was investigated. The results indicated that the **heat activation dramatically enhanced serpentine carbonation**. The best activation temperature was 650°C, at which the crystalline features were changed from lizardite to amorphous followed the decomposition of hydroxyl groups.

XI. Ho et al (2023). Using Clay to Capture and Store CO₂.

Ho, T et al (2023) reported that nanopores in clay not only reduced the energy barrier for the conversion of CO_2 to H_2CO_3 but also reversed the reaction from endothermic in bulk water to exothermic in nanoconfined water. While H_2O has no charge there is a slight negative charge in the region of the oxygen atom and a slight positive charge near the hydrogen atoms making it dipolar. They found that carbon dioxide is more stable in molecules such as the silicon-oxygen regions of the clay, than in the dipolar environment of water. As a result, water confined in clay nanopores absorbs more carbon dioxide than plain water does, and it takes less energy to convert carbon dioxide into carbonic acid. Instead of needing to then squeeze CO_2 out of the clay it could simply be stored in the clay, eliminating the need to bury it, as in standard DACS techniques. Since clay is inexpensive and abundant in nature and does not have to be mined and ground, as with ultramafic rocks, it could serve as an alternative to such rocks as a method of capturing and above ground storage of CO_2 . Further research will be necessary to evaluate the efficacy of this DAC technique.

XII. The Koornneef et al (2009) Study

Koornneef et al (2009) studied the percent of olivine reacted for different size particles of olivine ranging from 3 mm to 10 ums. Their results are shown as follows.



Relationship between reaction time and percentage of olivine reacted for various particle diameters. The rate of dissolution is assumed to be 6.0×10^{-8} moles/m²/minute and molar density is assumed to be 23,245 mol/m³. This is the dissolution rate that corresponds to a pH found in soil and rainwater (Hangx and Spiers 2009).

These results were calculated using the following formula.

$$1 - (1 - X)^{1/3} = \frac{R}{\rho * d} * t$$

X = fraction reacted	
R = rate of dissolution	$(6.0 * 10^{-8} \text{ moles} * \text{m}^{-2} * \text{minute}^{-1})$
$\rho = molar density$	(23245 mol/m^3)
d = particle size	(10, 30, 75, 100, 200 µm and 3 mm)
t = reaction time in minu	tes

Since these results are based on the reduction in size of the particles over time, the smaller the starting particle the faster it will progress. Using this equation showed that at a particle size of 1 um the dissolution goes to 90% completion in 18 days. These computer-based results involved no acid, no salt, no high temperatures and no concurrent grinding.

The following further illustrate the point. Weathering takes place on the surface. The surface area, $4\pi r^2$, of a **5 cm diameter olivine rock is 78.5 cm²**. If this is ground to 1 um diameter particles each particle would have a surface area of 0.000314 cm². Now the total

surface area is **250,875 times greater**. Clearly grinding climate rocks to 1 um diameter particles or smaller will dramatically increase the rate of weathering. This validates the International Program of **MINE**, **GRIND**, **SPREAD** and **SEQUESTER** outlined below.

XIII. Enhanced Weathering Conference (2022) presentations in Amsterdam May 4, 2022. The 26+ presentations can be seen by googling the conference and clicking on any of the 26+ presentations. There was considerable research and discussion of the potential of Ni toxicity in OAE. The following is a sampling of some of the presentations.

J. Guo: Investigating the effect of nickel concentration on phytoplankton growth to inform the assessment of ocean alkalinity enhancement.

• High concentration of organic ligands may reduce the Ni toxicity

- The Ni sensitivity is species specific
- The Ni tolerance of 11 tested species were surprisingly high

• The nitrogen sources, ligand concentration, and phytoplankton composition should be considered

• Applications of OAE with Ni-rich minerals may be safer in regions with high organic ligand and low urea concentrations

• More Ni impacts in coastal regions than in the open oceans.

Hu, Y.: Response of microbial community to olivine addition in coastal waters.

• Adding the olivine increased the seawater DSi by $8.6 \pm 0.1 \mu$ mol kg-1 in surface seawater within 10 days of incubation, and by $9.3 \pm 0.6 \mu$ mol kg-1 in bottom seawater.

• Meanwhile, the olivine addition increased the pH by 0.09 ± 0.02 in surface seawater and by 0.14 ± 0.02 in bottom seawater and increased the TA by $177 \pm 4 \mu mol \text{ kg-1}$ and $185 \pm 4 \mu mol \text{ kg-1}$ respectively.

Vicca, S. et al Bio-Accelerated Mineral Weathering.

• Significant increase in alkalinity in reactors with fungi and bacteria

Gerstman, K. Selling olivine for climate positivity.

• Their company Greensand is proposing many of the things we recommended in the Addendum such a selling ground olivine to people with gardens.

Summary So what have we learned from this extensive review? There are several lessons.

• Despite the rather voluminous literature on the dissolution and carbonation of ultramafic rocks, there have been remarkably few actual field studies of EW with olivine on croplands and even fewer of serpentine and basalt on croplands.

• There are even fewer studies that examine multiple variables such a particle size, olivine versus serpentine versus basalt, the need for pretreatments such as high temperature, high salt concentration, use of concurrent grinding, hot spots vs non-hot spots, and others.

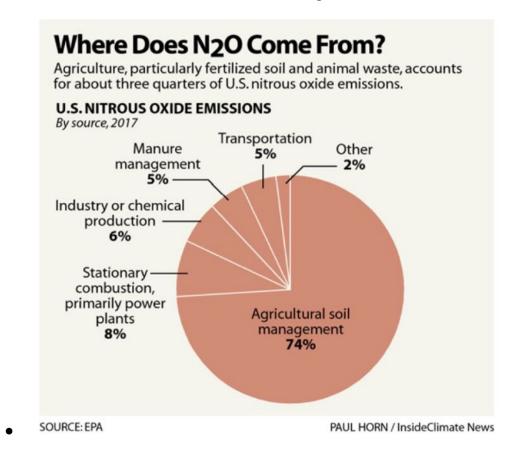
• There have been no studies comparing research field plots in temperate dry, versus temperate wet, versus tropical wet hot spot sites.

• Of all the physical or chemical enhancements <u>grinding to a fine size appears to be the</u> <u>simplest, must practical and most economical, especially if renewable energy is used</u>.

• Despite the many studies of the use of acid, salts, pressure, and other variables in the enhancement of ultramafic rock dissolution, <u>none of these seem suitable to EW on croplands</u>. As shown by Koornneef et al (2009) simply grinding to a 1 um size may be adequate for both olivines and serpentines.

Nitrous oxide N₂O

One pound of N_2O warms the atmosphere about 300 times the amount that one pound of carbon dioxide does over a 100-year timescale. Its potency and relatively long life make N_2O a dangerous contributor to climate change. It also depletes the ozone layer. As shown below, about three fourths of N_2O comes from the soil and agricultural sources.



In this regard it is of interest that a further co-benefit that may arise from the agricultural application of crushed silicate rocks to soils is suppressing emissions of the powerful and long-lived greenhouse gas N_2O and averting CO_2 emissions caused by liming. Liming with CaCO₃ can release CO₂ when it is applied to acidic soils (pH <6) typical of agricultural lands. In the USA, liming contributes 2% of agricultural greenhouse gas emissions.

Beerling, et al (2018) concluded that substituting a weatherable silicate rock, such as basalt, or silicate waste, for limestone, and increasing application rates over those used in

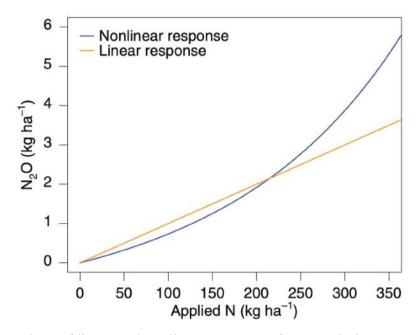
conventional liming operations, may offer a pragmatic, rapidly deployable global carbon cycle intervention strategy.

By increasing soil pH as they weather, silicates may also reduce emissions of N_2O , as found with liming (Gibbons, et al., 2014). Preliminary tests with a replicated field experiment support this suggestion with the soil N_2O flux from heavily fertilized maize plots decreasing by ~50% with the application 10 kg m² of pulverized basalt with no effect on soil respiration (Kantola, 2016). Thus, <u>basalt-treated arable fields may lower the current substantial global</u> soil atmosphere flux from croplands of 4-5 Tg N₂O N/yr as a by-product of weathering.

Agriculture is the main source of anthropogenic N₂O emissions, primarily through the application of synthetic nitrogen (N) fertilizers and manure on agricultural land. As the global amount of fertilizer used is expected to increase considerably over the next few decades, it is essential to establish reliable inventories of N₂O to define effective mitigation strategies (Makowski, D. (2019). Writing in *Nature Climate Change*, Thompson, and colleagues (2019) present **new global estimates of N₂O emissions and show that this greenhouse gas has increased substantially since 2009, at a faster rate than expected**. Their result questions one of the main methods currently used for the inventory of N₂O emissions at the global scale.

To mitigate N_2O emissions effectively, we must first understand their origin (Makowski, (2019). Emissions of N_2O to the atmosphere are mostly caused by nitrification and denitrification reactions. In terrestrial ecosystems, the driving processes are soil microbial activities, which are influenced by both natural factors and human management, in particular the application of synthetic and organic fertilizers. Soil N availability plays a key role in these processes, and N_2O emissions accelerated steadily during the twentieth and twenty-first centuries with the increasing use of nitrogenous fertilizer in crop fields. N fertilization is now recognized as a major source of anthropogenic emissions of N_2O , having contributed significantly to global warming.

In the bottom-up IPCC approach, the hypothesis of a linear relationship between N_2O emissions and applied N fertilizers has been questioned in several field studies. Instead, there may be a nonlinear response, with an acceleration of emissions as N application increases, probably because a higher proportion of N goes unused by crops in the case of high doses of fertilizer.



Comparison of linear and nonlinear response of N₂O emission to applied N. The linear response tends to underestimate emission for high levels of applied N.

Thompson and colleagues (2019) used a top-down method based on atmospheric measurements. Here the level of increase was substantially higher than previous estimates — more than double that of the IPCC default approach — indicating a faster N_2O growth rate than expected.

The results also revealed contrasting emission trends among regions. **Emissions** increased sharply in China and, to a lesser extent, South Asia, and Brazil. These results are consistent with the large increases in N inputs and surplus N in crops that have occurred in these regions over the past two decades. On the other hand, N₂O emissions remained stable in the United States and Europe over the same period. Thus, a substantial decrease in N₂O emissions could occur if these regions avoided excessive N fertilization. This will require international agreements. Of additional interest, the microorganisms of some remote lakes emit as much nitrous oxide as a megacity (Hao Kong et al (2023).

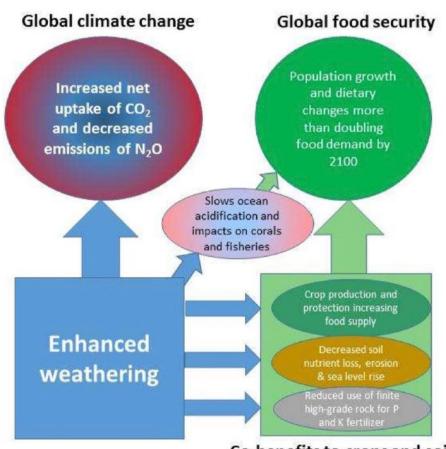
Breider, et al (2019) showed that when pH was reduced, the N₂O production rate during nitrification measured at subarctic stations increased significantly while nitrification rates remained stable or decreased. Contrary to previous findings, these results suggest that the effect of ocean acidification on N₂O production during nitrification, and nitrification rates are probably uncoupled. Collectively, these results suggest that <u>if seawater pH continues to decline at the same rate, ocean acidification could increase marine N₂O production during nitrification in <u>the subarctic North Pacific by 185% to 491% by the end of the century.</u></u>

Enhanced weathering of cropland both decreases the production of N_2O by cropland and combats ocean acidification which has a secondary effect of decreasing the marine production of N_2O . Thus, **this approach could decrease** N_2O both on land and in the sea.

Advantages of Enhanced Weathering on Cropland

An additional consideration relating to the overall outlook of EW is the recent report by Bellamy and Geden (2019) who argued that contrary to widely held assumptions, **methods for CO₂ reduction do not have to be deployed at large global scales to be relevant for climate policy.** Regarding governance, they suggest that it will primarily emerge 'bottom up' with companies, cities and countries utilizing these techniques and not be comprehensively coordinated 'top down' globally. Namely, since many NETs involve individual countries and areas, any governance should be local (ground up) and not globally (top down) (Lenzi, 2018). Such local governance will be small scale. Another way of putting it is every little bit helps – monitor the bits locally. This is consistent with our goal of having NGOs and non-profits participate in the extraction of CO₂ from the atmosphere (see below).

A summary of the advantages of crop weathering is shown below.



Co-benefits to crops and soils

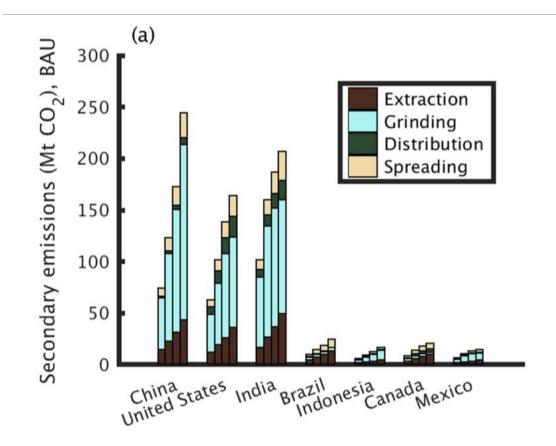
From Beerling, et al (2018)

More broadly, if proven effective, and undertaken carefully to minimize undesirable impacts, enhanced weathering may have untapped potential for addressing the United Nations **Sustainable Development Goals** (SDGs) adopted by 193 countries in 2015. For example, we highlight how sequestering CO₂ constitutes action on climate change (SDG 13), restoring soils and promoting sustainable agriculture contributes to zero hunger (SDG 2), helping protect the oceans from acidification conserves global resources in life below water (SDG 14), reducing agrochemical usage and recycling wastes helps with sustainable consumption and production (SDG 12), and improving agricultural production and restoring degraded soils contributes to land sparing (SDG 15) (see above figure).

Following the Beerling et al (2018) paper in *Nature*, two articles appeared in the July 9, 2020, issue *Nature*. The primary article was again by Beerling et al, (2020) entitled "Potential for large-scale CO_2 removal via enhanced rock weathering with croplands." It was accompanied by a News and Views comment on the Beerling paper by Lehmann and Possinger (2020) entitled "Atmospheric CO_2 removed by rock weathering." Combined, this was a real boost for EW.

Costs of EW

Beerling et al, examined the potential of different countries to use EW. They concluded that EW would cost, on average, US\$160–190 per ton of CO₂ in the United States, Canada, and Europe, and 55-120 per ton of CO₂ in China, India, Mexico, Indonesia, and Brazil. Furthermore, the authors report that China, the United States, and India — the three largest emitters of CO₂ from fossil-fuel use — have the highest potential for CO₂ removal using this method. One of their important conclusions was the relative cost of extraction, grinding, distribution and spreading. In the figure below, the Y axis was in terms of secondary emission (i.e., carbon cost) of these four processes. While not directly related to cost, it was a reasonable estimate of cost.



This showed that the cost of grinding contributed significantly to the total cost of this NET. Hangx and Spiers, (2009) examined the costs of grinding by size of the eventual product.

Energy	Costs f	for G	rindir	ng Oli	vine	
•						

	8
Crushing size	energy consumption
uM	kWh/ton olivine.
1000	4.94
300	8.17
100	13.40
37	23.71
10	173.71

Getting to a size of 1 um would be even more costly. The intriguing aspect of these analyses is that **the use of dedicated clean energy sources could significantly reduce the cost of this NET**. It is of interest that **Terrestrial Energy anticipates that their small, modular Integrated Molten Salt Reactor will be approved in Canada by 2025 and in the US by 2030.** These are super-safe reactors and could totally remove the CO₂ costs of grinding olivine and other minerals. Solar could also work (see below). Other nuclear options are available.

Hartmann et al, (2013) examined the issue of the relative cost of different methods of grinding in terms of energy use and produced the following Table 4.

TABLE 4.	Typical Energy	Requirements for	Various Crushing	g Technologies
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Crushing and Grinding Technology	Feed Particle Size (µm)	Product Particle Size (µm)	Capacity (t h ⁻¹)	Energy Use (kWh t ⁻¹)
Roller mills	104-105	18-65	12-225	6.6-11.0
	20-30	7–12	15-65	7.6-36.0
Centrifugal mills	11	1-2		150.0
Ball/stirred media mills	150	<37	0.1-35 ^a	13.0-233.0 ^a
Impact crushing	$10^4 - 10^5$	$10^2 - 10^3$	130-1780 ^b	20–100 ^b 0.6–1.5 ^b
Cone crushing	10 ⁵	$10^2 - 10^3$	80-1050 ^b	0.3-1.5 ^b
Jaw crushing	10 ⁵ -10 ⁶	10 ³	60-1600 ^b	1.0-1.4 ^b

^aIndicative values derived from Kefid technical data sheets.

^bIndicative values derived from Metso technical data sheets.

Sources: Wang and Forssberg [2003], Lowndes and Jeffrey [2009], Fuerstenau and Abouzeid [2002], O'Connor et al. [2005].

The often-recommended size of ground particles suitable for EW is 1 um. As shown above centrifugal and ball mills are the only methods listed to achieve this size, and they are the costliest, in terms of energy use. The placement of a Molten Salt Reactor or other small reactor at a centralized site, such as Twin Sisters (see below) would allow carbon free grinding to 1 um size prior to distribution of the ground ultramafic rocks.

The cost of transport is also an important issue. The following table 5, also from Hartmann (2013), that provides an estimate of relative transportation costs.

Freight/Haulage Transport Method	gCO ₂ Emissions km ⁻¹ t ⁻¹		
Airfreight	602		
Road heavy goods vehicle	62		
Diesel rail	15		
Electric rail	14		
Inland waterways	31		
Large tanker	7		

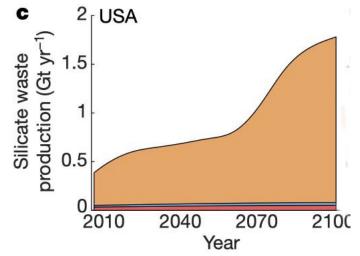
TABLE 5. Emissions From a Range of Freight Transport

Sources: McKinnon and Piecyk [2009], McKinnon and Piecyk [2010], Institution of Mechanical Engineers [2009].

Obviously, transporting by air would be prohibitively expensive while transport by large tanker is the least expensive. This bodes well for the possibility of transporting olivine from Norway to the US or other countries, or from the U.S. (Bellingham, see below) to other countries. The most likely form of transport in the U.S. would be by rail which is fairly low in expense. Recall the huge amount of coal transported by rail in the U.S.

Strefler, J. et al (2018) showed that enhanced weathering is an option for carbon dioxide removal that could be competitive at \$60 US/t of CO₂ removed for dunite, but at \$200 US/t CO₂ removed for basalt. The potential carbon removal on cropland areas could be as large as 95 Gt CO₂ /yr for dunite and 4.9 Gt CO₂/yr for basalt. The best suited locations are warm and humid areas, particularly in India, Brazil, South-East Asia, and China, where almost 75% of the global potential can be realized.

An additional reduction of costs could come from reducing the extraction part using products of various industrial processes. For example, the use of artificial silicon and calciumrich cements used in construction and the by-product of slag from steel manufacturing could provide and important source of these materials. It was predicted that these sources of silicates would increase over the century (see figure below).

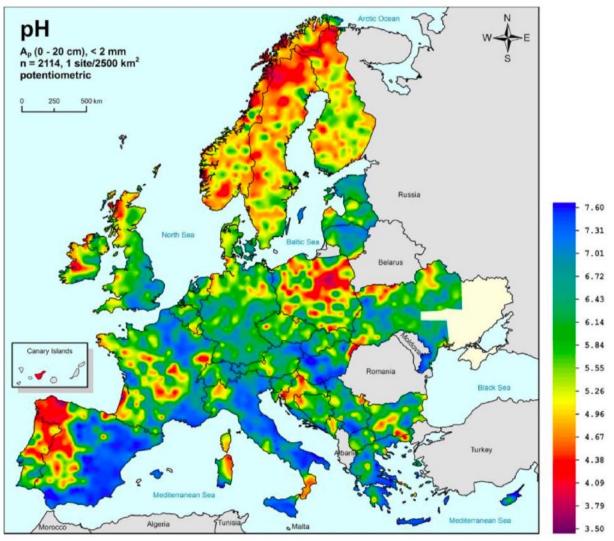


Forecast of increases in national bulk silicate production over the next century. Simulated future increases in bulk artificial silicate by products: slag, cement, kiln dust and cement demolition waste (orange), slag and kiln (blue) and slag (red). production during the twenty-first century are given for the USA.

Soil pH

Increasing soil pH alone by adding mafic rocks, would substantially boost crop yields in many regions of the world, because it is possible that **low pH decreases crop production on more than 200 million hectares of arable and orchard soils** (von Uexküll & Mutert, 1995). This area is equivalent to about 20% of the total extent of these soils (967 million hectares). Consequently, **on a global scale, acidity is the most important soil constraint for agriculture** (Wood, et al, 2000).

The following map illustrates the marked variation in soil pH, in this case in Europe (Fabian et al (2014).



Maps of pH in GEMAS soil samples for agricultural soil across Europe (Fabian et al., 2014).

Co-deployment of enhanced rock weathering with other soil-based sequestration approaches might both reduce limitations and maximize synergies (Amann & Hartmann, 2019). It was proposed that carbon markets might be required to help finance this, and other, approaches (Lehmann and Possinger, 2020).

The note by Lehmann and Possinger included a photograph showing what the process of spreading finely ground basalt would look like.



Application of silicate material to cropland (Lehmann and Possinger, 2020).

Biocatalysts

Living organisms can play a significant role in rock weathering. In nature, microbes, plants, lichens, and fungi contribute to rock weathering (Gadd, 2007). Sclarsic (2021) reviewed many different bioengineering approaches to catalyzing rates of weathering.

Fungi One approach was the use of fungi. The rock-inhabiting fungi *Knufia petricola* was shown to increase olivine dissolution rates by ~700% (Pokharel et al., 2019).

Cyanobacteria Another approach was the used of cyanobacteria. They can use photosynthetic energy to drive active uptake of carbon dioxide by ultramafic rocks, which creates an alkaline environment that favors carbonate precipitation (Riding, 2006). The ability of microbes to create both acidic and alkaline micro-environments could be harnessed in a co-culture to further increase weathering reaction rates.

Silicase. Microbes or fungi could potentially be engineered to release silicases optimized for rock weathering, perhaps in a semi-enclosed system analogous to a raceway pond or a stirred tank bioreactor to allow enzymes to become concentrated in a liquid medium. Once silica is released from rock however, it can linger as an amorphous silicon layer (SAL) on the rock surface, thus impeding further reactions (Pokharel et al., 2019). Some organisms disrupt the SAL through physical and chemical means that effectively creates holes through which dissolution reactions can continue to occur on fresh silicate. The fungus *K. petricola* is thought to attach to the silicon amorphous layer and exude protons, which penetrate the SAL and replace Mg+ in olivine, thus furthering olivine dissolution (Pokharel et al., 2019).

Carbonic anhydrase can be added to reactors to combine CO₂ with brucite Mg(OH)₂ to produce MgCO₃. This was shown to increase carbonation rates by up to 240% (Power et al., 2016).

Reducing Emission of CO₂ from Soil

With all the reports on the role of proper soil practices to sequester CO_2 , it may come as a surprise that the estimated **annual flux of CO₂ from soils to the atmosphere is estimated be 65** to 79 Pg C/yr (79 gigatons C/yr). Approximately 10% of the atmosphere's CO₂ passes through terrestrial soils each year. At a global scale, rates of soil CO₂ efflux correlates significantly with temperature and precipitation.

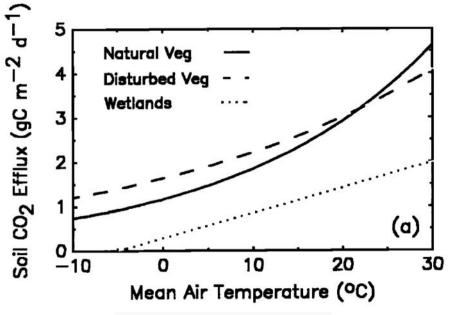
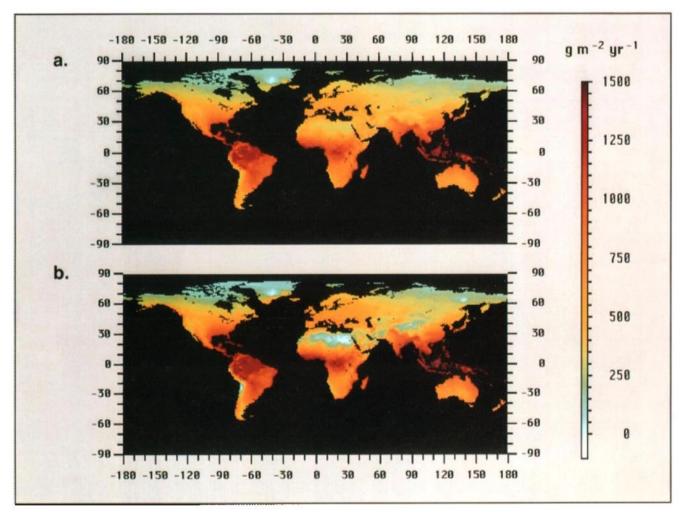


Figure from Raich & Potter, 1995

As shown in this figure, there is a 5-fold increase in soil efflux of CO_2 from 0 to 30 °C. Thus, clearly soil CO_2 fluxes have a pronounced seasonal pattern in most locations, maximum emissions coincide with periods of active plant growth. Their models suggest that **soils produce** CO_2 throughout the year and thereby contribute to the observed wintertime increases in atmospheric CO_2 . (Raich and Potter, 1995).

It is clear from the above, that there will be marked differences in the rate of CO₂ emissions by geographic region. This is illustrated in the following figure.



Global annual soil CO_2 emissions as predicted by the (a) log-transformed model A and (b) the untransformed model B, including corrections for wetlands (models C and D, respectively). Raich and Potter, (1995).

It is of interest that this map correlates closely with the map below of Hartmann et al (2009a) showing a published weathering hot spot map for the world. This suggests that the use of EW in these areas would be particularly productive.

Soil organic matter contains a large reservoir of carbon. Recently estimated at -1,600 Pg more than twice the atmospheric CO₂-C pool. Changes in the size of the soil C pool therefore can significantly affect atmospheric CO₂ concentration. In fact, concern has been raised about the potential for global warming to increase rates of CO₂ production by soils, thereby exacerbating the CO₂ loading of the atmosphere and providing positive feedback to climate warming (see references in Raich and Potter (1995). It is another tipping point.

Ray et al (2020) state the **soil is a source and a sink of CO₂ exchange**. A study in Texas showed that agricultural management practices influence soil water dynamics, as well as carbon cycling by changing soil CO₂ emission and uptake rates. The rate of soil CO₂ emission varied for different crops and different organic fertilizers (Ray et. al. 2020). The higher the amount of

organic fertilization (chicken manure, dairy manure, and Milorganite) the higher the CO₂ emissions.

The above represents the emission side of the soil story. Also of importance is the side of the equation wherein **proper soil management sequesters CO₂** (Paustian et al, 2007). Given the magnitude of the emission of CO_2 from soils, the use of EW on soils should significantly mitigate that.

Reducing CO₂ Efflux from Rivers

Liu et al (2022) reported that 112-to 209 million tons of CO_2 are taken up from the soil and then emitted into the atmosphere from streams and rivers each month worldwide, or 1.3 to 2.5 gigatons of CO_2 per year. They provided maps showing where this emission is the greatest. This is an enormous amount of CO_2 emissions to go unaddressed. While the following statement will need verification, it is likely that the **use of EW on the lands drained by these rivers showing the greatest efflux, is the only NET that can address this huge source of CO_2 emissions**.

Can a Carbon Capture Apparatus be Married to an Olivine Mine?

Klaus Lackner demonstrated a **moisture swing sorbent cycle for capturing carbon dioxide (CO₂) from air.** The sorbent, an anionic exchange resin, has been shown to absorb CO_2 when it is dry, and to release it again when exposed to moisture. By Lackner's calculation, each air capture device would be about 1,000 times more effective than a single tree.

Currently Lackner prefers to form the white resin into a honeycomb pattern—like thousands of straws stacked atop each other with the wind blowing through the holes. Their approach of what to do with the CO_2 is CCU - Carbon Capture and Use. While several such uses have been proposed it is doubtful that there enough uses to sequester billions of tons of CO_2 . They also proposed mineralization as a safe and permanent disposal of carbon dioxide and suggested using olivine or serpentine.

Obviously, if a concentrated stream of CO_2 was used, mineralization of olivine should be much more efficient than exposure to the atmosphere. This raises the possibility of placing a number Lackner type apparatuses, i.e., **DACS with Climeworks and Carbon Engineering, at an olivine mining site would avoid the cost of transporting olivine to croplands**. Research is necessary to determine how and if it is possible to marry carbon capture devices (Lackner, Climeworks, other) to olivine mining sites. The Lackner moisture sensitive resin would seem to require far less energy to release the CO_2 that other methods, and thus cheaper. This would avoid the potential problems with underground storage of CO_2 .

This concept can be further expanded to **A Three-way Hybrid of DAC, EW and OAE** (p 273).

Use of Tailings for EW

Ex situ mineralization can involve exposing reactive rock and minerals, alkaline industrial wastes, or mineral wastes from mining operations (**tailings**) to CO_2 on the earth's surface. This process can be facilitated by crushing and grinding reactive feedstocks to fine grain sizes and either spreading it across a surface or transporting it to pressure vessels where it can react with CO_2 . Several byproducts of industrial processes that provide opportunities for

carbon mineralization include cement kiln dust, waste concrete, fly ash, mine tailings, alkaline waste from paper mills, red mud, iron, and steel slag.

The following table from Li et al (2018) reviews some of the sites in the U.S where tailings have been used for carbonation.

Mining Deposits	Majority Minerals	CO ₂ Source	Rock Pretreat	Carbonation Method	Ref.
American Chrome, QC	Serpentine	Flue gas	TA	DC gas-solid	[99]
Old ilmenite mine, QC	Anorthite	Flue gas	NA	DC gas-solid DC aqueous	[100]
Okanogan nickel deposit, WA; Thompson nickel bell, MB	Serpentine	Pure CO ₂	TA, CA	DC aqueous	[64]
American Chrome, QC	Serpentine	Flue gas	TA	DC aqueous	[67,101]
Black Lake mine, QC	Serpentine	Flue gas	TA, MS	DC gas-solid	[102]
Lonmin Platnum mine, South Africa	Enstatite, plagioclase feldspar	Pure CO ₂	CA	IDC aqueous	[70]
Nickel Slag, New Caledonia	Olivine, serpentine	Pure CO ₂	TA, CA, MA	DC aqueous	[74]
Turnagain deposit, BC	Olivine, serpentine	Pure CO ₂	NA	DC aqueous	[103]
Turnagain deposit, BC	Olivine, serpentine	Pure CO ₂	MA	DC aqueous, DC gas–solid	[104,105]
Troodos ophiolite complex, Cyprus	clinopyroxene, anorthite	Pure CO ₂	MA	DC gas-solid	[106]
Black Lake mine, QC; Dumont Nickel project QC	Chrysotile, lizardite	Flue gas	NA	DC gas-solid	[66]
Thetford Mines, QC	Chrysotile	CO ₂ mix	TA	DC gas-solid	[63]
Hitura nickel mine, Finland	Serpentine	Pure CO ₂	CA	IDC aqueous	[107]

Table 1. Summary of current studies on ex-situ mineral carbonation of mine waste materials.

Note: TA is thermal activation, CA is chemical activation, MA is mechanical activation; MS is magnetic separation, NA is not applied, DC is direct carbonation, IDC is indirect carbonation.

Romanov et al (2015) reviewed all the relevant research about different types of tailings and reported a marked increase within the last few years in research into utilizing industrial waste streams as a source of Ca and Mg cations available for carbonation. Interest for using industrial residue materials and byproducts as reactant mineral carbonation sources has arisen because they are readily available, cheap, and often generated near large CO₂ emission sources. Fly ash and bottom ash from furnace operations typically contain a significant amount of lime (CaO) and magnesium oxide (MgO), which are more readily carbonated than the silicates. As shown by Fakhraee et al (2022, 2023) CaO and MgO are far more effective in OAE than olivine.

Their **small particle sizes of tailings would also facilitate rapid reaction rates**. Cement kiln dust and waste concrete, mining waste, slags from iron and steel-making operations, and alkaline paper mill waste are also promising feedstock material for carbonation. The capacity to sequester CO₂ with these alkaline residues depends directly on the proportion of divalent cations bound in oxides (CaO and MgO) and/or hydroxides Ca(OH)₂ and Mg(OH)₂ present in the waste matrix.

Among the solid residues generated by **municipal solid waste incineration (MSWI) bottom ash** accounts for 20–30% by mass of the original waste and tends to have **lower CaO and higher SiO₂ content compared to fly ash**. Accelerated carbonation has been proposed as an application for this ash prior to its final disposal. There are multiple advantages to carbonating MSWI ash. First, the ash contains a high CaO content. Secondly, MSWI ash already consists of fine-size particles and thus is ready for carbonation with no pre-treatment. Thirdly, the incineration process generates a significant amount of CO_2 , so alternately sequestering a portion of the CO_2 along with the waste products would be advantageous. Fourthly, carbonating the ash tends to decrease the leaching of potentially hazardous heavy metals contained within the ash. Using this resource could compensate for the CO_2 emitted when it is produced.

Fly ash is the finely divided residue that results from the combustion of pulverized coal and is transported from the combustion chamber by exhaust gases into the air. Over 61 million metric tons of fly ash were produced in 2001.

Renforth (2019) reported that 7 billion tons of alkaline materials are produced globally each year as a product or by-product of industrial activity. The aqueous dissolution of these materials creates high pH solutions that dissolves CO_2 to store carbon in the form of solid carbonate minerals or dissolved bicarbonate ions. Renforth showed that these materials have a carbon dioxide storage potential of 2.9–8.5 billion tons per year by 2100, and may contribute a substantial proportion of the negative emissions required to limit global temperature change to <2 °C.

A listing of these sources is as follows:

Material	2010 CO ₂ intensity ^a	2050 CO ₂ intensity ^b	Carbonation potential ^c	Measured carbonation ^d	Enhanced weathering potential ^e	Carbon offset recycling/reuse ^f
Blast furnace slag		2700-4300	413 ± 13	90-230	620 ± 19	~100. Up to 700 in high
Basic oxygen furnace slag Electric arc furnace slag	12,000	(286-1080) ⁱ	402 ± 17 368 ± 10	50-540	602 ± 25 552 ± 15	substitution specialised cements.
Ordinary portland cement	800	200-400 (100-200) ⁱ	510	300	773	-
Cement kiln dust	6900g	1700-3500	330 ± 12	82-260	530 ± 21	~0 Recycled into kiln
Construction and demolition waste	_		77-110	-	110-190	<5 As aggregate
Lime	1000	200 ^h	777 ± 13		1165 ± 19	—
Ultrabasic mine tailings	8-250	-	40-250	<50	60-377	-
Hard coal ash Lignite ash	20,000	(2000-2600) ⁱ	36 ± 6 146 ± 28	20-30 230-264	73 ± 10 246 ± 52	
Marine algae biomass ash			31		348	
Wood/woody biomass ash			-89-815		-118 to 1766	~100. Up to 700 in high
Herbaceous and agricultural biomass ash	490	<-16,200	-239-520	80-380	-323 to 1505	substitution specialised cements
Animal biomass ash ³⁸			56-376		145-724	
Biomass average			186 ± 126		461 ± 260	
Red mud	5400	(1080)	47 ± 8	7-53	128 ± 18 < 440 with acid neutralising capacity of liquor	-

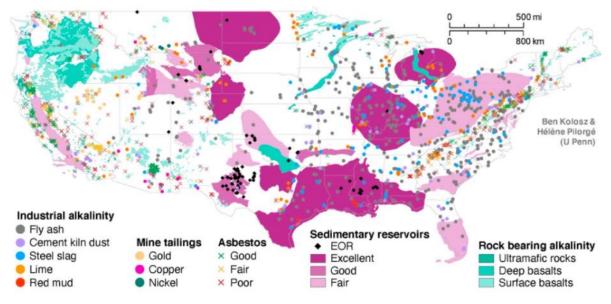
^hBased on an 80% emission reduction target²⁶ (e.g., UK and EU)

Accounting for aggregate primary energy carbon intensities in RCP2.6 by 2050. Brackets denote 2100 projected

Blondes et al, (2019) In a U.S. Geological Survey Scientific Investigations Report 2018-5079 entitled *Carbon Dioxide Mineralization Feasibility in the United States*, Blondes et al (2019) provided detailed maps on the location of sites for mafic and ultramafic mineral is the U.S. In addition, as shown below, they provided a detailed report on the use of **tailings in the U.S.** Mafic and ultramafic mine tailings are generated during the extraction and production of asbestos, chromite, diamond, nickel, platinum-group metals, and talc. These tailings react passively with atmospheric CO₂ to produce carbonate minerals under natural conditions (Levitan and others, 2009; Wilson, Dipple, and others, 2009; Wilson, Raudsepp, and others, 2009; Pronost and others, 2012). Piping CO₂ into the tailings and designing tailings storage methods to favor increased reactions would significantly increase the carbonation reaction rate (Gerdemann and others, 2007; Harrison and others, 2013; Power and others, 2013; Power and others, 2014). Power and others (2014) and references therein reviewed strategies to increase tailings-hosted reaction rates, including bioleaching.

In the United States, large amounts of mine wastes composed of ultramafic rocks and serpentinite rock have been left behind at abandoned asbestos mines, which could offer potential sites and sources of material for pilot projects of *ex situ* CO₂ mineralization. Prominent examples occur in Vermont and California (Krevor and others, 2009), such as the abandoned Belvidere asbestos mine near Eden Mills in northern Vermont and the former asbestos mines of the Coalinga mining district in San Benito and Fresno Counties of west-central California. The relevant references can be found in that report.

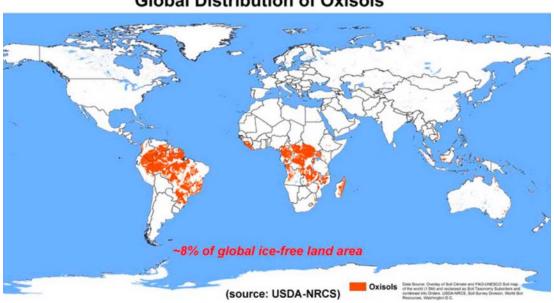
EFI (2020c) (Energy Futures Initiative) Rock Solid: Harnessing Mineralization for Large-Scale Carbon Management. This report included a map of the location of tailing sites relevant in the US.



There are clearly a large number of tailings sites.

Oxisols and Ultisols

Oxisols (from French *oxide*, "oxide") are very highly weathered soils that are found primarily in the tropical regions of the world.

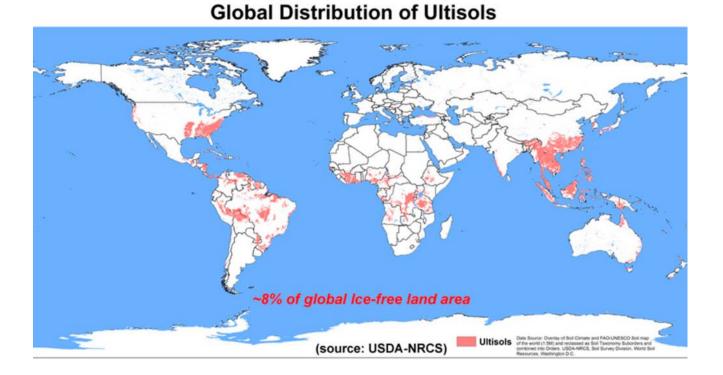


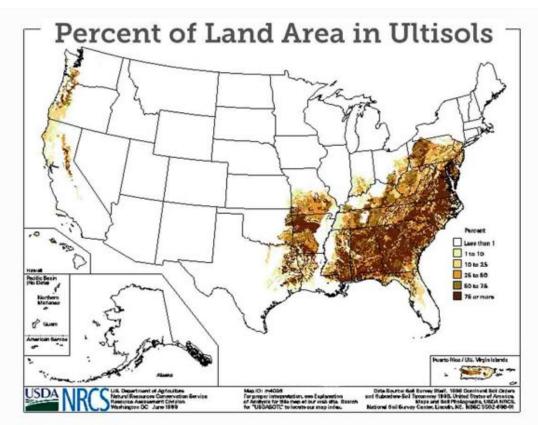
Global Distribution of Oxisols

These soils contain few weatherable minerals and are often rich in Fe and Al oxide minerals. Most of these soils are characterized by **extremely low native fertility**, resulting from very low nutrient reserves, high phosphorus retention by oxide minerals and low cation exchange capacity (CEC). Most nutrients in Oxisol ecosystems are contained in the standing vegetation and decomposing plant material. Despite low fertility, **oxisols can be quite productive with inputs of lime and fertilizers. Oxisols occupy approximately 7.5 percent of the global ice-free land area**. In the U.S., they only occupy approximately .02 percent of the land area and are restricted to Hawaii.

Ultisols (from Latin *ultimus*, "last") are strongly leached, **acid forest soils with relatively low native fertility.** They are found primarily in humid temperate and tropical areas of the world, typically on older, stable landscapes. Intense weathering of primary minerals has occurred, and much Ca, Mg and K has been leached from these soils. Ultisols have a subsurface horizon in which clays have accumulated, often with strong yellowish or reddish colors resulting from the presence of Fe oxides. The "red clay" soils of the southeastern United States are examples of ultisols.

Because of the favorable climate regimes in which they are typically found, ultisols often support productive forests. The high acidity and relatively low quantities of plant-available Ca, Mg and K associated with most ultisols make them **poorly suited for continuous agriculture without the use of fertilizer and lime**. With these inputs, however, Ultisols can be very productive. **They occupy approximately 8.1 percent of the global ice-free land area** and support 18 percent of the world's population. **They are the dominant soils of much of the southeastern U.S. and occupy approximately 9.2 percent of the total U.S. land area**.





The above was based on information from University of Idaho, College of Agricultural and Life Sciences, Twelve Soil Orders.

These areas are also referred to as **laterite soils**, which are formed **under conditions of high temperature and heavy rainfall with alternate wet and dry periods**. This leads to leaching of soil, leaving only oxides of iron and aluminum. It lacks fertility due to a lower baseexchanging capacity and a lower content of nitrogen, phosphorus, and potassium (Leonardos et al, 1987).

The distribution of oxisols and ultisols is highly relevant to the subject of Enhanced Weathering of croplands for several reasons.

- 1. It shows those areas of the world and U.S. that would benefit the most form EH of croplands.
- 2. Enhanced weathering with mafic and ultramafic are very effective in treating acid ultisols.
- 3. Many of these areas are also close to sources of mafic and ultramafic rocks, significantly reducing transportation costs.

4. World-wide it shows a remarkable similarity between the distribution of weathering hot spots (see above) and areas of oxisols and ultisols. Thus, the areas that need mafic and ultramafic rocks as fertilizer and the areas of weathering hot spots are very similar. This is because the very factors that make hot spots, e.g., warm temperatures and high rainfall, also cause oxisols and ultisols. Initially focusing on these areas for the application of mafic and ultramafic rock would make the process far more efficient.

What About Methane?

The contribution of other GHGs, besides CO₂, together account for about 34% of radiative forcing. Even <u>if all excess anthropogenic atmospheric CO₂ were removed</u>, <u>radiative forcing would only be reduced by half</u>. Methane emissions from ruminants contribute roughly 120 MtCO₂ equivalents per year in the United States. Methane leaks from oil wells account for a similar amount. Our proposals on how to decrease methane emphasizes decreasing emissions. This **plan is covered in the section below on Federal Help**.

Direct Capture of N₂O

Just as methods are available for the direct capture of CO_2 from the atmosphere, the same is true for N_2O . Jang et al, (2021) present an energy-efficient clathrate-based greenhouse gas-separation (CBGS) technology that can operate at room temperature for selectively recovering N_2O from gas mixtures. The government should explore this approach to this critical need.

Map of Ultramafic sites in US.

An evaluation of the scale of major CO_2 point sources and their proximity to the potential mineral sources resulted in the identification of 7 primary ultramafic mineral carbonation regions within the conterminous U.S. is shown on the following map.



Ultramafic Mineralization Carbonation sites. Regions 1 and 5 contain olivine; regions 2-4 contain lizardite serpentine; region 6 contains antigorite serpentine; and region 7 contains wollastonite. 5 = Asheville Mining District

This map differs in many details from the above **EFI (2020c)**. We would urge the U.S. Geological Survey to clarify this.

How are Weathering Hot Spots Identified?

Tropical areas are weathering hotspots because high forest primary production and warm, wet climates promote mineral weathering. While Taylor et al (2016) identified weathering hot spots as areas where the cumulative CO_2 consumption is between 3 and 4 $1og_{10}$ mol CO_2 /meter, how is this CO_2 consumption determined? Three 2009 papers by Hartmann (Hartman et al, 2009 a, b; Hartmann, 2009) provide the answer. These areas are determined by two different approaches:

i) a reverse approach based on hydro-chemical fluxes from large rivers and

ii) a forward approach applying spatially explicit a function for CO_2 consumption. Here a CO_2 consumption model, trained at high resolution data, was applied to a global vector based lithological map with 15 or more lithological classes. The calibration data were obtained from areas representing a wide range of weathering rates.

The authors used this latter technique which has far greater resolution. The results highlight the role of hotspots (> 10 times global average weathering rates) and hyperactive areas (5 to 10 times global average rates) (Maybeck et al 2006). Only 9 % of the global water runoff area is responsible for about 50 % of CO₂ consumption by chemical weathering. If

hotspots and hyperactive areas are considered: 3.4% of water outflow surface area corresponds to 28% of global CO₂ consumption.

Regions dominated by volcanos are hyperactive or even "hot spots" in relation to dissolved silicon (DSi) mobilization (Hartman et al, 2009). Many of the "hottest" spots are found in Southeast Asia. Some of these hotspots coincide with, or are near to, tropical peat swamp forests in coastal Sumatra, Malaysia, and Borneo, which are also global biodiversity hotspots currently under pressure from logging, fire and land use change. As shown in the above figure, there are also hot spots in Central and South America.

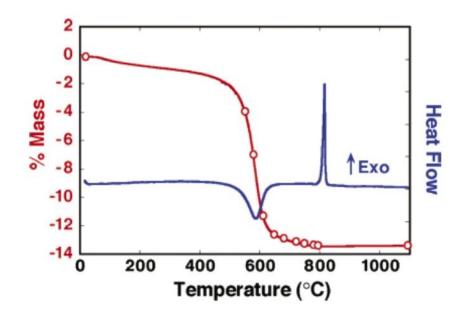
Adding Serpentine to the Soil – Is that a Problem?

Note that the above studies involved adding olivine and other non-serpentized rocks to the soil. While the dissolution of olive on croplands has been occasionally studied, the problem is most ultramafic rocks are serpentized and the **rate of dissolution of serpentine is orders of magnitude slower than olivine** (Daval, 2013). Much of that literature relevant to accelerating the dissolution of ultramafic rocks including serpentines is aimed at the commercial extraction of magnesium, or the extraction of CO_2 from flue gas produced by coal fired power plants. The following table from Azadi et al (2019) illustrates the different methods that have been used to enhance the rates of dissolution.

Strategy	Reference	Method	Benefit		
Mechanical pretreatment of serpentine rock	[62-66]	High-energy crushing and grinding	Increases the overall specific surface area of the minerals, i.e., the surface per unit mass available for Mg/Ca-extraction		
Thermal activation of the [67–73] Heating the mi hydrated Mg-silicate serpentine above		Heating the mineral to 630 °C or above	Destabilises the crystal lattice, thus increasing the reactivity of the mineral Heat activation also creates an even higher specific surface area [46]		
Increasing reaction temperatures	[74,75]	Applying operating temperatures above 100 °C	Accelerate the kinetics of the reaction		
Increasing reaction pressure	g reaction pressure [76,77] Applying operating CO ₂ pressure above 150 bar		Increases the activity of protons needed for metal extraction. Also counteracts the low solubility of CO ₂ at high temperature		
Using organic and inorganic chemicals			Enhances the kinetics of the carbonation process and precipitation of magnesium carbonate		
Applying New double-step and multistep process designs	[81]	The operating conditions are changed between the different stages	Allows to control and promote extraction and precipitation separately		
Direct capture of CO ₂ from flue [81,82] as stream		Capturing CO ₂ directly from a flue gas stream by mineral carbonation	Provides a simple and straightforward process route		

Table 1. Strategies and methods used to increase the speed and efficiency of the carbonation reaction.

All of these methods are quite energy intensive leading many to question their applicability to the whole problem of CO_2 sequestration. The use of heat has been one of the most frequently sites techniques. The following diagram from McKelvy et al (2004) shows the dramatic increase dissolution of lizardite, a serpentine rock Mg₃(Si₂O₅)(H₂O)₄, at 600°C.



Simultaneous thermogravimetric (TGA) and differential thermal analysis (DTA) of Philips lizardite from ambient temperature to 1100 °C.

As described previously, the general formula for the serpentines is Mg, Fe, Ni, Al, Zn, $Mn)_{2-3}$ (Si,Al,Fe)₂O₅(OH)₄. The serpentine clay minerals are Lizardite, Atlantisite and Infinite, with the chemical composition of Mg₃Si₂O₅(OH)₄. They differ in color and where they are found. Lizardite is the most common and most often used in research studies.

In California for the Del Puerto Ultramafic body ranges from 10 to 90 percent olivine while in Wilbur Springs the percent olivine ranges from 60 to 100% (Goff and Lackner, 1998). One solution for serpentines is preheating of the rock, but this is very energy inefficient (Tebbiche, et al, 2021). Krevor and Lackner (2011) reported that the rate of dissolution of serpentine is three orders of magnitude faster in the presence of citrate ions, but it is doubtful that this can be used economically at large scale. Dissolution is also pH sensitive, increasing with lower pH, but adding various acids is also economically inefficient. As reviewed above, grinding to a small particle size may be the best way to accelerates the reaction.

The Basics of CO₂ and Ocean Chemistry (Harvey, 2008)

The emission of CO₂ into the atmosphere from human activities leads to an increase in the partial pressure of atmospheric CO₂, and in response to this, there is a net flow of gaseous CO₂ into the **surface layer** of the ocean. Once dissolved in surface water, CO₂ combines with water to form a weak acid (carbonic acid, H₂CO₃), which then dissociates to bicarbonate (HCO₃) and carbonate (CO₃²⁻) ions. The reactions are:

- $1 \qquad \qquad CO_2 + H_2O \rightarrow H_2CO_3$
- 2 $H_2CO_3 \rightarrow H^+ + HCO_3^-$
- 3 $CO^{2-} + H^+ \rightarrow HCO_{3^-}$

4 (net reaction) $H_2O + CO_2 + CO_3^2 \rightarrow 2HCO_3^-$

Reaction (2) would tend to increase the acidity of seawater as CO_2 is added, except that CO_3^{2-} consumes the H⁺ that is released by reaction (2), so that there is no change of pH if the occurrence of reaction (2) is balanced by reaction (3). The carbonate ion thus acts as a buffer, inhibiting changes in pH to the extent that it is available. However, the supply of CO_3^{2-} in the surface layer of the ocean is limited, so as more CO_2 is absorbed by the ocean, the H⁺ concentration (and hence acidity) of ocean water increases.

At the same time as ocean acidity increases, the concentration of CO_3^{2-} decreases. CO_3^{2-} is a constituent in CaCO₃ (calcium carbonate), which occurs in two mineral forms: used as the structural material of corals and pteropods (high-latitude zooplankton), and calcite, used as the structural material of the foraminifera (animals ranging in size from less than 1 mm to several centimeters) and coccolithophores (a group of phytoplankton). Also, many echinoderms and mollusks and some crustaceans contain calcareous shells or exoskeletons.

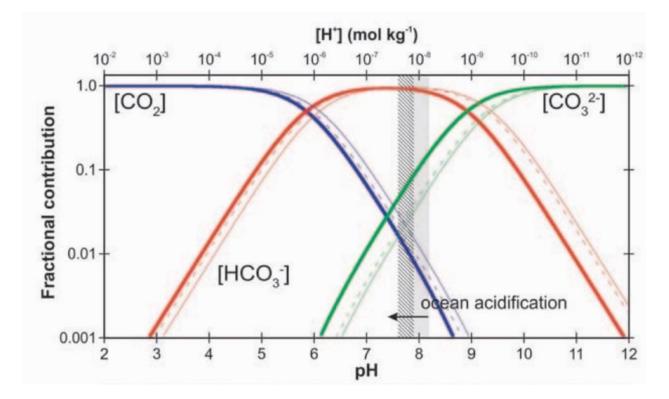
Although calcareous plankton account for only a few percent of marine primary productivity, calcareous organisms occur throughout the marine food chain, while **coral reefs are thought to shelter over two million species of marine life.** The **surface waters of the oceans are presently supersaturated with respect to both forms of calcium carbonate**, a condition that is essential for the growth and health of calcareous organisms. However, the absorption of CO_2 by the oceans reduces the degree of supersaturation by reducing the carbonate (CO_3^{2-}) concentration. These decreases in the supersaturation with respect to calcite and aragonite are likely to have profoundly negative impacts on marine ecology.

The carbonate concentration required for supersaturation increases with increasing pressure and hence with increasing depth in the ocean. As a result, deep ocean waters are unsaturated with respect to CaCO₃, and carbonate sediments produced by the downward rain of dead calcareous plankton accumulate only on the shallower ocean floor (above depths ranging from about 0.3 km to 4 km). Over a period of several thousand years, the decrease in CO_3^{2-} concentration as the ocean absorbs anthropogenic CO₂ will induce the dissolution of the deepest carbonate sediments, as water that had been supersaturated becomes unsaturated. This will restore the CO_3^{2-} that had been depleted from ocean water, neutralize the increase in acidity of ocean water, and allow the ocean to absorb further CO₂ from the atmosphere over a period of several thousand years. The whole process can be sped up if finely ground limestone, which is overwhelmingly CaCO₃, were to be sprinkled into the surface layer of the ocean and allowed to sink into unsaturated deep water, where it would dissolve. Seawater with restored CO_3^{2-} could be available to absorb more atmospheric CO₂ within as little as a few years after the addition of CaCO₃.

Harvey (2008) stated their results suggested that ground CaCO₃ could be effectively applied at a rate of 4 billion tons/yr (0.48 Gt C/yr) producing an eventual rate of absorption of CO₂ of about 0.27 Gt C/year a (1 billion t CO₂/year). This would represent 5 to 10 percent of the total sequestration of CO₂ needed.

Bjerrum Plot for Carbonate Systems

To obtain an estimate of the relative amounts of the carbonate cycle that are in sea water at a given pH we turn to a Bjerrum plot named after Niels Bjerrum. It is a graph of the relative concentrations of the different species of a of the carbonate cycle in a solution, as a function of pH, when the solution is at equilibrium. Due to the many orders of magnitude spanned by the concentrations, they are commonly plotted on a logarithmic scale.



To determine the ratio of CO₂, HCO₃⁻ and CO₃²⁻ to each other, run a straight line up from any pH. For example, **at ocean pH of about 8, approximately .93 or 93% are in the form of HCO₃⁻**, 0.08 or 8% is in the form of CO₃²⁻ and 0.01 or 1% is in the form of CO₂. The solid bars are at temp = 25°C and salinity = 35%. The other lines are for different conditions. The hashed region represents the ocean pH in 2010. The grey region is the ocean pH years prior to 2010.

From the above it can be seen that the ability of seawater to buffer changes in its pH as CO_2 is added depends on the amount (or concentration) of CO_3^{2-} present. Note that as CO_{2aq} increases CO_3^{2-} decreases. The buffering capacity of seawater will decrease as more CO_2 is added and CO_3^{2-} is progressively consumed. Because of this, the proportion of CO_2 added to seawater that remains as CO_2 (aq) increases as more CO_2 is added, an effect first recognized by Roger Revelle and Hans Suess (Revelle & Suess 1957) and quantified as the 'Revelle Factor'.

The proportion of DIC present as CO_2 is also affected by temperature. The consequence of this is that, as the ocean warms, less DIC will be partitioned into the form of CO_2 (and more as CO_3^{2-}), hence enhancing the buffering and providing a 'negative feedback' on rising atmospheric CO_2 . Well-known positive feedback in the carbon cycle arises due to the decrease in solubility of CO_2 gas in seawater at higher temperatures. In fact, this greatly outweighs the negative feedback described above, meaning that <u>as the ocean surface warms, even more of</u> the emitted fossil fuel CO_2 will remain in the atmosphere.

By way of conclusion, Revelle remarked that "Human beings are now carrying out a large-scale geophysical experiment of a kind that could not have happened in the past nor

be reproduced in the future." This sentence has since been quoted more than any other statement in the history of global warming, (Roger Revelle's Discovery, 2021).

In summary, before scientists would take green-house effect warming seriously, they had to get past a counterargument of long standing. It seemed certain that the immense mass of the oceans would quickly absorb whatever excess carbon dioxide might come from human activities. Roger Revelle discovered that the peculiar chemistry of seawater prevents that from happening. His 1957 paper with Hans Suess is now widely regarded as the opening shot in the global warming debates (Roger Revelle's Discovery, 2021).

Two years later, two scientists in Stockholm, Bert Bolin, and Erik Eriksson (1959), explained the seawater buffering mechanism in clear terms and emphasized what it meant. Unlike Revelle and Suess, they used an ocean model in which, correctly, <u>only the top two</u> <u>percent, mixed quickly with the atmosphere, which made it that much slower for the great</u> <u>bulk of the oceans to absorb the gas.</u> Bolin and Eriksson also predicted unequivocally an exponential climb of industrial production and used that to calculate that atmospheric CO₂ would probably rise 25% by the end of the century. Revelle had already guessed that there might be a 25% increase by 2000. It reached that mark in 2010. <u>The community of geophysicists began to grasp that we could not rely on the oceans to absorb all our emissions of fossil fuels.</u> However, OAE may help to overcome that.

Putting Ultramafic Rocks in the Ocean (OAE)

The essence of this approach is that by adding calcium and magnesium to the ocean, the CO_2 dissolved in the ocean can mineralize and form carbonate minerals, reducing amount of CO_2 in the water and disturbing the equilibrium. This will cause more CO_2 to leave the air and enter the ocean (Woodall et al, 2021). Since this leads to an increase in alkalinity and a decrease in acidity, this process is called **Ocean Alkalinity Enhancement or OAE** (NAS, 2021). A 2023 book by Oschlies, et al (2023) provides a review of many aspects of OAE.

An alternative way to put it is that the limits imposed by needing to avoid large shifts in pH in freshwater (river) systems using EW on land might be avoided by dissolving olivine in the ocean where much larger volumes of water are involved and the concentration of dissolved silicon (DSi) is well below the saturation level (Köhler et al., 2013; Hartman et al, 2013).

Thus, **direct dissolution of olivine in the open ocean would significantly increase the realistic scope of Enhanced Weathering with olivine (or other minerals)** (NAS, 2019). The CO₂ sequestration per amount of olivine being dissolved is slightly smaller if olivine is dissolved in the ocean compared to on land, but this effect is relatively small, and the benefit would be a faster rise in surface ocean pH, a very welcome outcome for counteracting ocean acidification. However, surface ocean pH is approximately 7.8–8.3, and dissolution would proceed at a much slower rate than in tropical seas, thus requiring smaller mineral grain sizes for comparable dissolution rates relative to the application of the minerals onto soils. Moreover, potential complications such as the settling of grains into the deep ocean prior to their complete dissolution would have to be carefully assessed (Hartman et al, 2013).

Based on the discussion of total alkalinity (TA) at the beginning of this section, the input of Mg^{2+} and Ca^{2+} leads to an immediate increase of TA. The "one-time-input" weathering of 10 Gt olivine (e.g., pure forsterite (Mg₂SiO₄) would result in an input of 1.4 x 10¹⁴ mol Mg²⁺. If this input were evenly distributed over the whole ocean surface (taken here as the upper 50 m of

the water column), the impact on TA and pH would be relatively small ($\Delta TA = 8 \text{ mmol kg}^{-1}$, $\Delta pH = 0.001$. (Hartmann, et al 2013). However, changes in TA and pH would increase over time **if the same amount of olivine was added every year over a longer period**. If the "one-time-input" is restricted to a much smaller volume the local changes in TA and pH would be much higher ($\Delta TA = 790 \text{ mmol kg} \lambda 1$, $\Delta pH = 0.11$ for 1% of the upper ocean volume). The extent of the change in TA and pH in the surface ocean over time will depend in part on circulation and mixing and thus must be calculated using an ocean circulation model.

Governance issues relating to OAE are discussed by Burns and Corbett (2020) and Webb et al, (2021). Under international law, countries typically have jurisdiction over activities within 200 nautical miles of their coastline. In the U.S., coastal states typically have primary authority over areas within three nautical miles of the coast, and the federal government controls U.S. waters further offshore. At the international level, the most directly applicable instruments are **the Convention on the Prevention of Marine Pollution by Dumping of Wastes and Other Matter ("London Convention"), and the Protocol to that Convention ("London Protocol").** The London Convention gives parties broad authority to permit projects, provided they do not use certain, prohibited substances listed in the Convention. Parties to the London Protocol might not permit non-research ocean alkalinity enhancement. There is a great deal that can be done on a research basis including the design, building, and testing of ships designed for OAE using renewable energy. It is recommended that OAE researchers follow commonsense requirements such a minimizing pollution, obtaining a permit, and pursuing scientifically valid activities.

It is of interest that **Burns and Corbett (2020) argued that OAE was the NET with the** greatest potential in terms of carbon removal and its co-benefits.

OceanNET The EU-funded OceanNET, is a research project to explore the feasibility and positive and negative impacts of ocean-based NETs and demonstrate whether they can play a substantial and sustainable role in medium-to-long-term actions to limit warming. It brings together recognized NET experts from economic, political, legal, social, and the natural sciences. Total funding is 7 million euros. It had a start date of July 2020 and an end date of June 2025.

Studies of the OAE are reviewed below.

Ocean Alkalinity Enhancement (OAE) and Electrochemistry

Two types of electrolytic OAE (eOAE and heOAE) We use the shorthand term eOAE for electrolysis assisted OAE. There are two types of eOAE technologies - those that use add minerals such as olivine (eOAE) and those that do not (heOAE).

OAE refers to OAE that utilizes the addition of olivine or other minerals to the reaction mix. There are two types: **those that use carbonate minerals and those that use silicate minerals**.

First, three papers that discuss general aspects of OAE.

Albright et al (2016) quantified the net calcification response of a coral reef to alkalinity enrichment and showed that, when ocean chemistry is restored closer to pre-industrial conditions, net community calcification increases. The study was conducted on One Tree Reef a pseudo-atoll in the southern Great Barrier Reef off Australia.

Bach et al, (2019) examined the potential risks and co-benefits of OAE on marine pelagic ecosystems. The molecules or elements generated during chemical weathering of these minerals and sustained in solution comprise for major groups:

(I) Bicarbonate (HCO₃⁻) and carbonate ion (CO₃²⁻), summarized as "alkalinity",

(II) Silicic acid (Si(OH)₄) termed silicates,

(III) Certain alkaline earth metals like calcium (Ca²⁺) and magnesium (Mg²⁺) but potentially also alkali metals like sodium (Na⁺) and potassium (K⁺),

(IV) a variety of "trace metals" associated with the minerals such as iron (Fe^{2+} or oxidized aqueous species), and nickel (Ni²⁺).

Heavy metals will be a major subject as these elements may occur in high concentrations in basic and ultrabasic rocks (e.g., dunite), which are the most widely recognized source rocks for EW/OAE. If these have a toxic effect on marine life, this raises **the possibility of first removing them by electrolysis prior to placement in the ocean**.

The subject of heavy metals in EW and OAE is discussed in detail later (pages 229-241).

The authors stated that the most fundamental outcome of more than two decades of ocean acidification research is that carbonate chemistry perturbations affect calcifying organisms disproportionately. Thus, it is important to pay special attention to calcification when considering impacts of increased alkalinity on marine organisms and ecosystems. They concluded that calcifiers would profit in a scheme where CaCO₃ derivatives would be used. This may turn the blue ocean into a whiter ocean.

When using silicates, the release of additional Si, Fe and Ni could benefit silicifiers and N₂-fixers such as **cyanobacteria** and increase ocean productivity ultimately turning the blue ocean into a greener ocean. As to silicates, dissolving one mole of olivine leads to an increase in total alkalinity by 4 moles and for silicic acid (H₄SiO₄) by one mole. The maximum scale of mineral addition through OAE lies somewhere at **around 10 Gt/year** which is roughly 70 Tmol (trillion moles) of DSi (dissolved silica)/year, if dunite was used. Thus, OAE would be a source of DSi to the surface ocean that is 5-14 fold higher than all natural sources combined.

Goldberg, P. et al (2022) reiterated some of the advantages of OAE. First, they included the fact that carbonates have a lower energy state than CO_2 , which is why mineral carbonation is thermodynamically favorable and occurs naturally. Secondly, the raw materials such as magnesium-based minerals are abundant. Finally, the produced carbonates are unarguably stable. They reviewed the studies produced by the Albany Research Center (see above) to accelerate the rate of weathering. They also discussed plans to construct larger scale operating units to validate the method as a viable sequestration tool at industrially relevant scales. Raw materials for binding the CO_2 exist in **vast quantities across the globe**. Readily accessible deposits exist in **quantities that far exceed even the most optimistic estimate of coal reserves (~10,000 × 10⁹ tons).**

They also noted that the overall process is exothermic and, hence has the potential to be economically viable. In addition, its potential to produce value-added by-products during the carbonation process may further compensate its costs.

They also point out that there is approximately an order of magnitude more serpentine than olivine. While they identify the major problem as its slower weathering rate, as shown throughout this document, **grinding to a 1 um size**, using renewable energy, significantly increases the weathering rate for both olivine and serpentine without the need for high temperatures, and other impractical methods of accelerating weathering.

1. The Addition of Carbonate Minerals.

a. Carbonate rocks can be crushed and reacted with CO₂, such as at captured at power plants, to produce carbonic acid solution bicarbonate ions that would be released to the ocean (Rau and Caldeira, 1999, 2001; Rau, al, 2001; Caldeira and Rau, 2000; Rau, 2008). This is termed the carbonate-dissolution process.

 CO_2 rich exhaust gases from fossil fuel power plants when dissolved in seawater in a reactor vessel at the power plant would produce a carbonic acid solution H₂CO₃. Readily solubilized crushed carbonate rocks, such a CaCO₃, produces Ca²⁺ and 2HCO₃⁻

$$CO_2 + H_2O + CaCO_3 \rightarrow Ca^{2+} + 2 HCO_3^{--}$$

The latter is released back into the seawater where it is diluted. The added Ca++ results in an increase in alkalinity while the HCO_3^- which cannot directly interact with the atmosphere, thus sequestering carbon (Caldaria and Rau, 2000). Mann (2021) pointed out that the process of CO_2 capture at power plants is only 90% effective in capturing CO_2 , thus large amounts are still released into the atmosphere. Caldaria and Rau (2000) recognized this and stated that to attain 100% capture, additional methods would need to be added.

They reported that substantial infrastructure would be required to mine, transport, crush and dissolve these minerals plus substantial pumping for a large operation. The power plants would have to be located near the coast. They estimated a cost of \$68 per ton of C sequestered versus \$300 per ton for deep sea injection.

b. Alternatively, **Crushed carbonate minerals could be directly released into the** ocean (Kheshgi, 1995; Harvey, 2008). Carbonate minerals such as limestone could be heated to produce lime (Ca(OH)₂ which could be added to the ocean to increase alkalinity (Kheshgi, 1995). The problem with this is that it releases CO_2 to the atmosphere, thus cutting its effectiveness.

c. To avoid this release of CO₂ into the atmosphere, the splitting of calcium carbonate can be done electrochemically (House et al, 2007; Rau, 2008) as shown below.

2. The Addition of Silicate Minerals. Here there are two approaches.

a. Directly releasing pulverized silicate rocks into the ocean (Kheshgi, 1995) to increase alkalinity and drawdown of atmospheric CO_2 . Using carbonate or silicate mine **tailings**, which are already crushed to a small particle size is a viable alternative. Here energy requirements would be lower because of the small particle size, but little is known about trace contaminants in mine tailings that might be released (Renforth, 2017).

b. This process can also be enhanced electrochemically (House et al, 2007).

OAE using Electrochemistry and Added Minerals (eOAE)

As indicated above, electrochemical processes have been proposed for the enhancement of the use of both carbonate and silicate minerals in OAE. The use of electrochemistry has the following **advantages**.

- a) It has the potential of being the cheapest method of OAE.
- b) **If placed on ships** it can do OAE in many places thus speeding up its ocean wide dispersion.
- c) If placed on ships it can be used locally such as at the Great Barrier Reef to counter the destruction of the coral reefs.
- d) If placed on ships the using renewable energy could make the boats independent of needing to fill the tanks with fossil fuels.
- e) If placed on ships it could concentrate on areas of the greatest ocean to air emissions (out gassing) and areas of greatest utility for using OTEC as an energy source.
- f) If placed on ships it could be concentrated in the Southern Ocean and the Sub-polar Pacific Ocean, where the efficiency of the process is greatest (Burt et al (2021).
- e) If the electrolysis-GDA (gas diffusion anode) process is used it is up to 5 times more energy efficient than the Chloralkali process.
- f) If EW with the production of H₂ by Electrolysis is used it is up to 50 times more efficient than BECCS.
- f) The mafic rock was used would not have to be ground to a 1 um size, further saving energy.
- g) The above also apply to eOAE (see below).

So, how do these electrochemical processes work?

a. For Carbonate Rocks.

In the **Rau (2008)** article, *Electrochemical Splitting of Calcium Carbonate to Increase Solution Alkalinity: Implications for Mitigation of Carbon Dioxide and Ocean Acidity* described the process. The chemical reaction involved is:

 $CaCO_3 + 2H_2O + CO_2 + (DC \text{ electricity}) \rightarrow \uparrow H_2 + \uparrow 0.5O_2 + Ca^{2+} + 2(HCO_3^{-})$

Powdered CaCO₃ (limestone, chalk, dolomite) is added to the reaction mix. CaCO₃ comprises more than 4% of the earth's crust and is found throughout the world. It's inexpensive and occurs in common natural forms. It cannot be directly added to the ocean and be expected to take up CO₂ since that is the final form by which nature stored CO₂ in the ocean. However, when electricity is used in the presence of seawater, CO₂ is consumed (above). The reaction produces hydrogen and oxygen gas, Ca²⁺ and soluble bicarbonate (HCO₃⁻). The last two increase the alkalinity of the ocean which leads to increased CO₂ uptake and combats ocean acidification. The hydrogen and oxygen can be used in fuel cells to produce electricity thus taking some of the load off solar panels and wind turbines. In experiments by Rau (2008), after the electricity of this mix was turned on the pH of the solution increased from 8.0 to 9.0. in 1.5 hrs.

The electrolysis could be done directly in the ocean seawater where the electrodes and carbonate would penetrate the water surface from either stationary (e.g., docks, jetties, platforms) or mobile, piloted, or vessels (barges, ships, buoys, etc.). If non-fossil-fuel electrical power is generated on site using wind, solar and fuel cells, the electrochemical splitting of the carbonate could proceed on site without using fossil fuels and generate alkalinity directly into the ocean. Calcium carbonate (limestone) would need to be supplied at a rate of 1 mole of CaCO₃ per mole

of CO₂ consumed, or **2.3 tones per net ton CO₂ consumed**. (The molecular weight of CaCO₃ is 100.0 and of CO₂ is 44.0. 100.0/44.0 = 2.3).

The exact quantity would be dependent upon the purity and reactivity of the carbonate used. It would be of interest to determine how much of the electricity used for electrochemistry can be recovered with the fuel cells.

b. For Silicate Rocks

House et al (2007). In this article, *Electrochemical Acceleration of Chemical Weathering as an Energetically Feasible Approach to Mitigating Anthropogenic Climate Change*, the authors describe the process of removal of HCl from the ocean which liberates sodium hydroxide and thereby increases the alkalinity of seawater. This process enhances oceanic uptake of CO₂. Alternatively, NaOH and HCl can be produced via electrolysis of an artificial brine made from mined rock salt or from desalination plants. After neutralizing the HCl via **the dissolution of silicate rocks**, the dissolution products and the NaOH are added to the ocean to increase its alkalinity. The thermodynamics of the process that employs seawater are essentially the same as the process that employs an artificial NaCl solution. The steps of the process are as follows.

Step 1 involves the removal of chloride ions from a salt solution. This **Chloralkali process** is a standard electrochemical process for producing chlorine gas and hydrogen gas from NaCl and water.

 $NaCl + H_2O \rightarrow electricity \rightarrow NaOH + .5 Cl_2 + .5 H_2$

With modification this can be employed to produce Cl₂ and H₂ from seawater.

Step 2. $Cl_2 + H_2 \rightarrow 2HCl$

In this step H_2 and Cl_2 can also be used in a **special fuel cell** to produce electricity and HCl. (Thomassen, 2005).

Step 3. The HCl can be added to mafic rocks to produce $MgCl_2$ and SiO_2 which can be added to sea water to **increase alkalinity**.

$$HCl + MgSiO_3 \rightarrow MgCl_2 + SiO_2 + H_2O$$

Step 4 The NaOH can be used to capture and store CO_2 on land as well as alkalinizing the ocean.

$$CO_2 + NaOH \rightarrow NaHCO_3$$

Each mole of HCl removed from the ocean and neutralized increases ocean alkalinity by 1 mol, and on a time scale of about 100 years. Each additional mole of alkalinity causes \sim 1 mol of atmospheric CO₂ to dissolve into the ocean. The mixing processes will distribute the additional alkalinity into deeper water over hundreds to thousands of years, enhancing the current ocean uptake, which is approximately 7.5 gigatons of CO₂, (2 Gt C per year) (McNeil et al 2003).

These time scales for the ocean wide distribution of the alkalinity can be decreased by carrying out the electrolysis on ships that traverse wide swaths of the ocean. The authors listed a number of potential difficulties involved in bringing this process to scale.

Rau, et al (2013) experimentally demonstrated that direct coupling of **silicate** mineral dissolution with saline water electrolysis and H₂ production effected **significant air CO₂ absorption, chemical conversion, and storage in solution**. They observed as much as a 10^5 - fold increase in OH⁻ concentration with a **pH increase of up to 5.3 units**, relative to experimental controls following the electrolysis of 0.25 M Na₂SO₄ solutions when the anode was encased in powdered silicate mineral, either wollastonite or an ultramafic mineral. After electrolysis, full equilibration of the alkalized solution with air led to a significant pH reduction and as much as a 45-fold increase in dissolved inorganic carbon concentration. This demonstrated significant **spontaneous air CO₂ capture, chemical conversion, and storage as a bicarbonate, predominantly as NaHCO₃**. The excess OH⁻ initially formed in these experiments apparently resulted via neutralization of the anolyte acid, H₂SO₄, by reaction with the base mineral silicate at the anode, producing mineral sulfate and silica. This allowed the NaOH, normally generated at the cathode, to go un-neutralized and to accumulate in the bulk electrolyte, ultimately reacting with atmospheric CO₂ to form dissolved bicarbonate.

Using renewable electricity, optimized systems at large scale might allow relatively highcapacity, energy-efficient (<300 kJ/mol of CO₂ captured), and inexpensive (<\$100 per ton of CO₂ mitigated) removal of excess air CO₂ with production of carbon-negative H₂. Furthermore, when added to the ocean, the produced hydroxide and/or bicarbonate could be useful in **reducing sea-to-air CO₂ out gassing** and in neutralizing or offsetting the effects of ongoing ocean acidification.

Although silicate weathering is extremely slow under ambient conditions, silicate mineral dissolution and subsequent reaction with CO_2 can be significantly increased in strong acids and/or bases. Because very large pH gradients are produced in **saline water electrolysis cells** [anolyte pH < 2, catholyte pH > 12, it was reasoned that placing a silicate mineral mass in direct contact with such solutions would facilitate their dissolution to metal and silicate ions. Once formed, the positively charged metal ions could migrate to the negatively charged catholyte to form metal hydroxide, whereas the negatively charged silicate ions would react with the H+ rich anolyte to form silicic acid, silica, and/or other silicon compounds. Contacting of the produced hydroxide solution with CO_2 would lead to **CO₂ capture** and **storage as bicarbonate or carbonate**.

It was demonstrated that significantly elevated pH and hydroxide concentrations (relative to controls) can be attained in bulk electrolyte during the **electrolysis of seawater** (naturally containing 0.48 M NaCl) when the anode is encased in a porous carbonate mineral (CaCO₃) mass.

Such approaches have the **potential to be more energy-efficient and less environmentally risky than more widely discussed DACS**. This is because they avoid:

(i) energy-inefficient base/sorbent regeneration and production of highly concentrated molecular CO_2 and,

(ii) the need to guarantee safe long-term sequestration of CO_2 gas (see pages 23-26).

The mafic rock used was a serpentinized hornblende metaperidotite from the Canadian Shield containing 38.8% SiO2, 22.6% MgO, 12.5% FeO, 9.23% Al₂O₃, and smaller quantities of other constituents. The primary net reaction inferred was as follows:

 $2CO_2 + 2H_2O + MgSiO_3 + Na_2SO_4 + V_{DC} \rightarrow H_2 + .5O_2 + MgSO_4 + 2NaHCO_3 + SiO_2$ $V_{DC} = direct \ current.$

The ability to significantly enhance atmospheric CO₂ absorption into a salt solution with the strategic addition of silicate minerals and the application of DC electricity was demonstrated. One implication of the preceding observations is that globally abundant and relatively inexpensive silicate minerals, as well as natural or artificial brines, could be reacted using renewable energy to effect spontaneous capture of air CO₂ and its long-term storage as bicarbonate or carbonate. The cogeneration of valuable carbon negative H₂ and O₂ or Cl₂ could help offset costs or could allow some energy recovery, for example, via fuel cell conversion to electricity with the production of fresh water or acid (HCl). This could be neutralized by adding it to mafic rocks, as proposed by House et al (2017).

Regarding the energy and carbon penalty for mineral extraction, grinding, and transportation, several studies indicate that depending on the circumstances, these costs will be small relative to that for the electrolysis. This is predicated on the assumption that **grinding silicate minerals to extremely small particles** (e.g., 1 μ m Kohler et al, 2013) will not be required for the process. Significant amounts of preexisting waste silicate mineral particles and fragments (tailings) are also available at little or no cost at certain locations.

Methods of cost-effectively producing and using hydroxides in once-through schemes also allow the use of the massive air contacting offered by natural water bodies (e.g., the ocean), as opposed to reliance on expensive, engineered air contactors to effect air CO₂ absorption and chemical conversion to environmentally beneficial marine (bi)carbonates in solution at global scales.

Perhaps more significantly, the strategic addition of chemical base to the surface ocean in locations when/where the dissolved CO₂ concentration exceeds that in the overlying atmosphere e.g., **out gassing regions** (Takahashi T, et al. (2009). **This process could consume some of the excess dissolved CO₂, and thus avoid its out degassing to the atmosphere.** This would then reduce some of the ocean's CO₂ emissions back into the atmosphere per year (Prentice, et al. (2001), and hence proportionately reduce the CO₂ burden in the atmosphere without the need of performing the more difficult task of directly removing CO₂ from air. Furthermore, excess ocean CO₂ removal is required for any effective air CO₂ capture scheme because removal of air CO₂ alone will simply reduce air CO₂ flux, largely replacing the air CO₂ removed (Cao and Caldeira, 2010). Schemes that consume (Lampitt et al, 2008) or remove and sequester excess ocean CO₂ (Eisaman et al, 2012) therefore effectively address both excess ocean and air CO₂, reducing the need **for direct air CO₂ capture**.

Systems using seawater as an electrolyte would be optimally sited at coastal locations, where solar, wind, or ocean-derived electricity would also be locally available and where silicate mineral resources and H₂ markets are in proximity. The electrolysis could, in fact, be done directly in brine or seawater reservoirs or in the ocean, where the electrodes and silicate would penetrate the water surface from either stationary or mobile platforms (e.g., **modified or specially designed ships**). This would preclude the need and expense of pumping seawater into

electrochemical facilities on land but would also require sea-going infrastructure, maintenance, and resupply. Rau, et al (2013) discussed several issues relating to scaling up this approach.

Both proposals suggest that boats could be built or retrofitted to have electricity from on board solar, wind and fuel cells. Most of the time they are on the ocean there is no need for the speed that is provided by diesel engines. Thus, the diesel motors could be supplemented or replaced with **electric motors to minimize or eliminate the use of fossil fuels**. When docked they could be loaded with CaCO₃, other carbonate rocks or ultramafic rocks. If feasible, plans could be standardized for such vessels and each country with access to the ocean and ultramafic or carbonate rocks, could be encouraged to buy them. A world-wide fleet of several hundred such vessels might be needed. If each ship was capable of onloading, for example, 200,000 tons of rock, and dispersing it in a week to 10 days, then returning for more, each vessel could accommodate 7,300,000 tons of rock per year. A fleet of 100 such boats could accommodate .73 gigatons per year or approximately .30 gigatons of CO₂ per year, while a fleet of 1000 boats (see below) could sequester **3 gigatons/year**. While not the total answer to CO₂ capture it is good part of the solution and directly addresses ocean acidification.

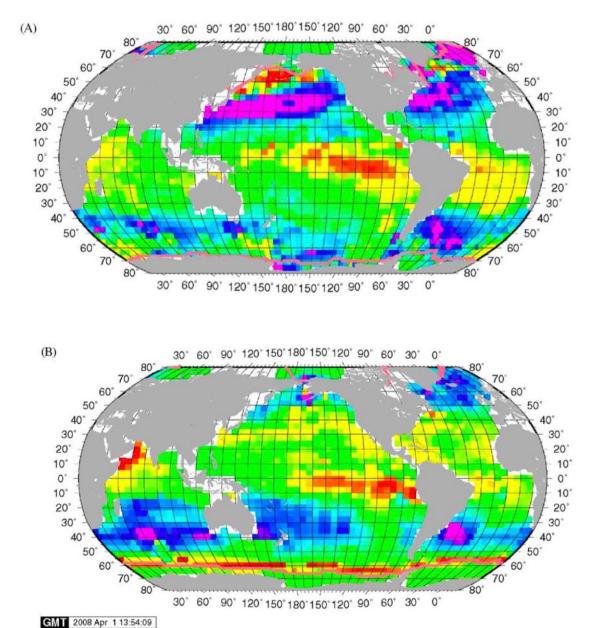
Caserini et al (2021) approached OAE by the spreading of Ca hydroxide (slacked lime). Based on maritime traffic data from the International Maritime Organization for bulk carriers and container ships, and assuming low discharge rates and 15% of the deadweight capacity dedicated for slacked lime transport, the maximum slaked lime potential discharge from all active vessels worldwide was estimated to be **between 1.7 and 4.0 Gt/year**.

A disadvantage of using slacked lime is that CO_2 is released during its production. To counter this, Caserini et al (2019) and Renforth and Henderson (2017) proposed methods of **producing slacked lime without producing CO**₂.

A summary of the US and world production of limestone, $CaCO_3$, is available from the USGS (2012). CaCO₃ also occurs as chalk and is mined in northern Europe from the southern UK to eastwards deep into Russia. Dolomite $CaMg(CO_3)_2$ is found in Midwestern quarries of the USA; Ontario, Canada; Switzerland; Spain and in Mexico, along with many other places in the world. There are many other types of carbonate minerals.

Ocean Upwelling (Outgassing) of CO2

It is correctly believed that the ocean adsorbs vast amounts of CO_2 . It is much less appreciated **that some areas of the ocean also release huge amounts of CO_2 back into the atmosphere**. If this **outgassing** can be significantly reduced, it would have a very positive effect on controlling global warming. Worldwide areas of upwelling are shown in the red and to a lesser degree the yellow areas in the following figure from Takahashi, et al (2009).



Legend for above figure. Climatological mean sea–air CO_2 flux (g-C/m²/month) in **February (A)** and **August (B)** in the reference year 2000. Positive values (yellow–orange-red) indicate sea-to-air fluxes, and negative values (blue–magenta) indicate air-to-sea fluxes. (Takahashi et al. 2002, 2009).

0

Net Flux (grams C m-2 month-1)

2

3

4 5 6

7

8 9

1

-2

-8 -7 -6 -5 -4 -3

-1

The areas of the greatest year-round out gassing of CO_2 back into the atmosphere are in the **Equatorial Pacific** west of Ecuador. In the winter (February) the major area is the **Arctic Ocean**.

In the summer (August) the major areas are the **Southern Ocean** around Antarctica and **Arabian Sea** next to Yemen.

Upwelling in the Equatorial Belt

Temperate and polar oceans of both hemispheres are the major sinks for atmospheric CO_2 , whereas **the equatorial oceans are the major areas for outgassing of CO_2** (Takahashi, T. et al, 1997; Boutin et al, 1999).

The equatorial areas of outgassing are between 14N to 14S and emit +0.7 Pg-C/y back to the atmosphere each year (Feely et al (2006). Here 0.7 Pg or pentagrams (10^{-15}) equals 0.7 gigatons (10^{-9}) of Carbon or 2.56 Gt (gigatons) of CO₂. If our goal initially is to remove 10 Gt of CO₂ from the atmosphere each year this would represent 25% of that goal, and this is just the equatorial area. The big question is: can local efforts from ship based OAE reduce this outgassing?

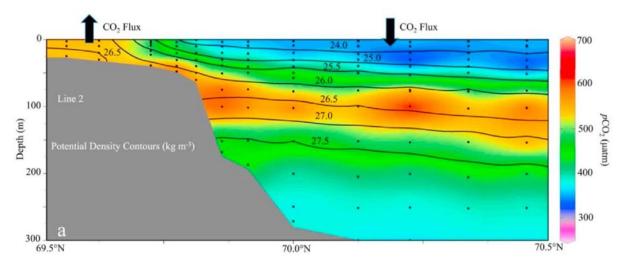
During non – El Niño periods the central and western equatorial Pacific is a major source of CO_2 to the atmosphere; it is near neutral during strong El Nino periods, and a weak source during weak El Niño periods (Feely et al (2006). El Niño events occur roughly once every 2 – 7 years and typically last about 12 – 18 months. The opposite phase of the cycle, called La Niña, is characterized by strong trade winds, cold tropical surface temperatures, and enhanced upwelling along the equator. The mean circulation of the equatorial Pacific Ocean is characterized by upwelling that brings cold nutrient- and carbon-rich water to the surface along the equator east of about 160°E during non–El Niño periods. The primary source of the upwelled water along the equator is the narrow Equatorial Undercurrent (EUC), which flows eastward across the basin (Feely et al (2006).

In the western equatorial Pacific, the variability in pCO_2 is also governed by the displacement of the boundary between warm pool waters, where air–sea CO_2 fluxes are weak, and equatorial upwelled waters which release high CO_2 fluxes to the atmosphere (Boutin et al, 1999).

Upwelling in Arctic (Mathis et al, 2012)

The continental shelves of the western Arctic Ocean play an important and likely increasing role in the global carbon dioxide cycle through complex and poorly understood interactions with sea ice, ocean and atmospheric circulation, and terrestrial processes (Bates et al., 2011). Recent studies in this region have shown significant warming of the atmosphere coupled with rapidly declining sea ice extent and thickness and increased storm activity.

In October 2011, persistent wind-driven upwelling occurred in open water along the continental shelf of the Beaufort Sea in the western Arctic Ocean. During this time, cold salty halocline water—supersaturated with respect to atmospheric CO_2 (p $CO_2 > 550$ matm) and undersaturated in aragonite (Omega aragonite < 1.0) was transported onto the Beaufort shelf. A single 10-day event led to the outgassing of 0.18–0.54 Tg-C and caused aragonite under saturations throughout the water column over the shelf. If we assume a conservative estimate of four such upwelling events each year, then **the annual flux to the atmosphere would be 0.72–2.16 Tg-C** which is approximately the total annual sink of CO_2 in the Beaufort Sea from primary production.



Cross-sectional plot of pCO_2 (matm) with density (kg/m³) contours along CTD (Conductivity Temperature Depth) line. The black arrows indicate the direction of the CO₂ flux (Mathis et al, 2012).

As sea ice retreat continues with global warming, and storms increase in frequency and intensity, further outgassing events and the expansion of waters that are undersaturated in carbonate minerals over the shelf are probable.

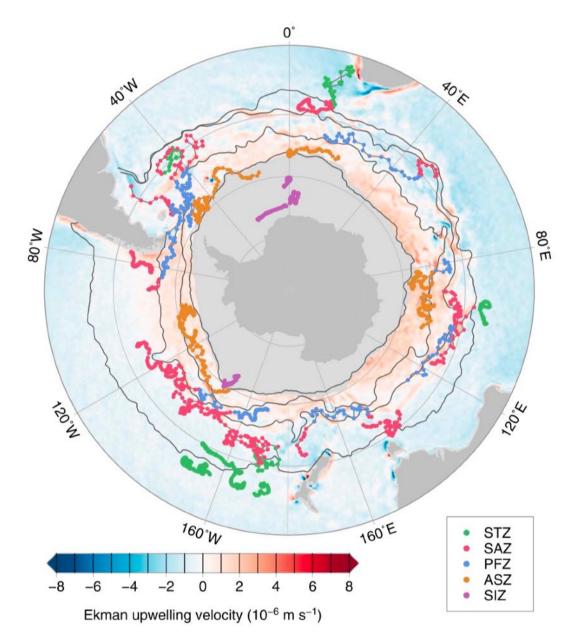
Since these upwelling events are natural occurrences, it is likely that this part of the western Arctic shelf has always been a larger source of CO_2 to the atmosphere than has previously been assumed. However, recent reduction in sea ice extent and duration, coupled with increased storm activity, has likely exacerbated the impacts of upwelling on water column saturation states and CO_2 flux across the air-sea interface.

Upwelling in the Antarctic - Southern Ocean

The ocean can act like a sponge for anthropogenic CO_2 because of the high concentration of carbonate ions, which react with excess CO_2 to form bicarbonate. That process keeps the oceanic CO_2 concentration low, and thus allows for more uptake. But as the ocean takes up more carbon, the carbonate ions are reduced, which reduces the ocean's ability to absorb CO_2 . As ocean surface temperature increases in the future, the solubility of CO_2 will decrease, which will, in turn, increase the oceanic partial pressure of CO_2 and decrease the rate of ocean carbon uptake. In short, those two processes lead to positive feedback on global warming: As the ocean warms, it removes less CO_2 from the atmosphere, which leads to increased warming (Morrison, et al, 2015).

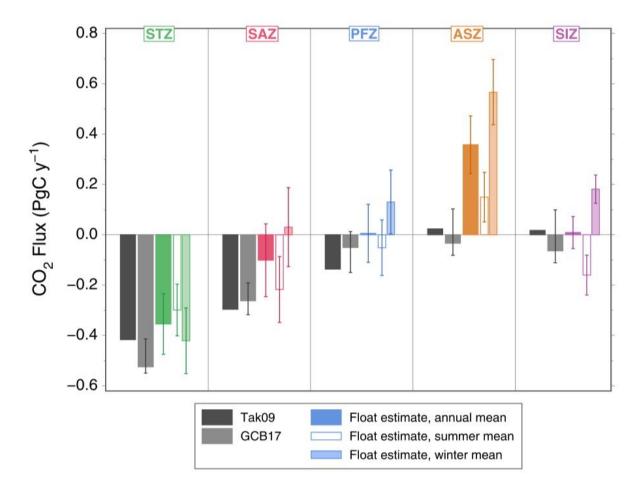
Simulation studies of Burt et al (2021) show that a **Southern Ocean application of OAE** is most efficient, sequestering 12% more carbon than the global OAE despite being applied across a surface area 40 times smaller. The **Sub-polar Pacific** is the next most efficient while the Sub-polar Atlantic is the least efficient. The sub-polar Pacific is close to the Twin Sisters site for mining climate rocks, described below (p 198).

So, how much outgassing of CO₂ occurs in the Southern Ocean and where? Precise answers to these questions were provided by Grey et al (2018). In their paper entitled *Autonomous Biogeochemical Floats Detect Significant Carbon Dioxide Outgassing in the High-Latitude Southern Ocean.* They set out 35 autonomous pCO₂ testing floats at the following locations in the Southern Ocean. This allowed measurements to be made throughout the year, and especially the difficult winter months.



Profile locations from 35 autonomous biogeochemical floats deployed in the Southern Ocean from 1 May 2014 through 30 April 2017, colored according to zone. Dark gray contour lines show the boundaries of the five regions used in the analysis. Background colors show the annual mean wind-induced upwelling velocity, calculated from the Scatterometer Climatology of Ocean Winds (Risien & Chelton, 2008), with light gray indicating the region covered by both seasonal and permanent sea ice in that climatology. STZ = Subtropical Zone; SAZ = Subantarctic Zone; PFZ = Polar Frontal Zone; ASZ = Antarctic-Southern Zone; SIZ = Seasonal Ice Zone.

First, the background colors show that the maximum upwelling velocity is close to the land mass of the continental Antarctica (pink). The following figure shows the positive CO_2 flux (outgassing) and negative flux (CO_2 adsorption) for the five different zones.



Annual net oceanic CO₂ flux (Pg C/year) estimated from float data (solid colors) and from two ship-based estimates, Tak09 (dark gray) and GCB17 (light gray), calculated by sampling the gridded estimates at the same locations as the floats. The mean float-based estimates calculated for May–October (winter) and for November–April (summer) are shown by the narrow bars. **Positive indicates net outgassing (ASZ)**. Negative indicates uptake. See above for abbreviations.

This shows that the greatest outgassing of CO_2 occurs closest to the coast of Antarctica, (ASZ zone). Thus, approximately **0.5 PgC or 0.5 gigatons of C**, or **1.8 gigatons of CO₂** are out gassed around Antarctica each year.

Arabian Sea (Verneil et al, 2021)

The Arabian Sea (AS) is a region of the ocean that has been found to naturally release CO_2 to the atmosphere (Sarma et al., 1998), mitigating the ocean's role in moderating

atmospheric CO₂ accumulation. While the AS regional basin is considered too small to greatly impact global budgets of air-sea CO₂ exchange it attracts attention because some of the highest rates of air-sea CO₂ flux and values of partial pressure of CO₂, or pCO₂, have been observed there, in addition to unique features such as the world's thickest oxygen minimum zone (OMZ) and corresponding Carbon Maximum Zone (CMZ) (Paulmier et al., 2011). A potential advantage of performing OAE in the Arabian Sea is that **Oman, a major source of ultramafic rocks is very close by.**

Verneil et al, (2021) found that the Arabian Sea emits $\sim 160 \text{ TgC/yr}$, which equals 160 megatons C/y, which equals 587 megatons CO₂/yr or **0.59 gigatons CO₂/yr**.

In his 2008 article *Mitigating the atmospheric* CO_2 *increase and ocean acidification by* adding limestone powder to upwelling regions **Harvey suggested that the** <u>outgassing of CO₂ from the ocean could be mitigated by the direct application of CaCO₃ to the relevant</u> <u>regions of the ocean.</u> "If this were done in regions where the saturation horizon is shallow and where strong upwelling (>50 m/a) occurs (the two conditions tend to be correlated with one another), water with restored CO_3^{2-} could be available to absorb more atmospheric CO_2 within as little as a few years after the addition of CaCO₃."

If we assume that the Arctic and Antarctic outgassing areas are too difficult to reach, that leaves 0.59 gigatons CO₂/yr for the Arabian Sea and 2.56 Gt (gigatons) of CO₂/yr for the Equatorial Zone or a total of 3.15 Gigatons CO₂/yr that could be amenable to partial reduction by localized OAE. If OAE was successful in reducing this by half, this would be 1.6 gigatons of CO₂/yr or 16% of the goal of 10 gigatons of CO₂/yr. If it reduced outgassing by 80% that would equal 2.5 gigatons CO₂/yr or 25% of the goal of 10 gigatons CO₂/yr. If OAE could be placed on ships that could sail the Arctic and Antarctic areas of outgassing, even larger amounts of outgassing could be prevented.

c. Electrolysis-GDA (gas diffusion anode)

Davies et al. (2018) discuss using the brine produced from desalination plants as a source of MgOH₂ for alkalinization of the ocean. Seawater brine contains significant amounts of metal ions which have potential to combine with and sequester CO_2 as carbonate or bicarbonate. This approach is to convert the magnesium chloride in seawater brine to magnesium oxide or hydroxide, which has similar absorptive capacity for CO_2 as calcium oxide as proposed for ocean liming.

Recently, advanced electrochemical methods have been developed to improve seawater brine electrolysis. For example, **Xie et al.(2013)** introduced a new way of decomposing magnesium chloride by an electrolysis process incorporating a gas diffusion anode (GDA), yielding magnesium hydroxide and hydrochloric acid. This electrolysis-GDA method is particularly appealing in terms of its potentially low energy consumption and simpler configuration of the electrolysis cells. These would be the key factors in keeping both capital and operational costs low for large scale processing. The following diagram illustrates the apparatus.

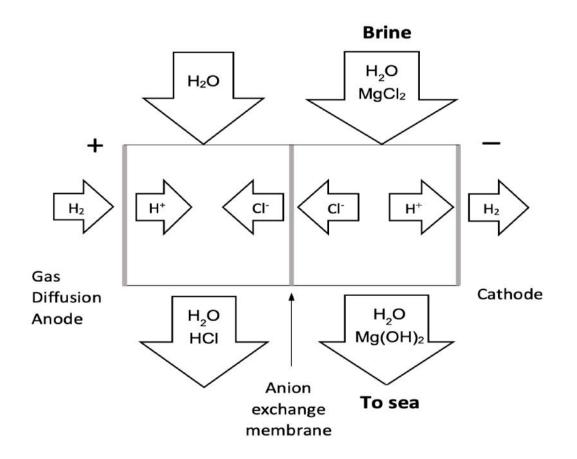


Illustration of the electrolyzer with **gas diffusion anode (GDA)** for splitting brine containing magnesium chloride into HCl and Mg(OH)₂. Modified from Xie et al (2013). Davies' objective was to estimate the energy and water requirements of such NET-desalination, and to compare these penalties to the other NETs based on values provided in the literature.

With use of the GDA, the two half-cell reactions are:

Cathode: $Mg^{2+} + 2H_2O + 2e \rightarrow Mg(OH) + H_2$ Anode: $H_2 + 2Cl^- + 2e \rightarrow 2HCl$

The overall electrolysis reaction is accordingly:

 $MgCl_2 + 2H_2O \rightarrow Mg(OH)_2 + 2HCl$

Magnesium hydroxide reacts stoichiometrically with CO₂ in seawater to form magnesium carbonate:

$$Mg(OH)_2 + CO_2 \rightarrow MgCO_3 + H_2O$$

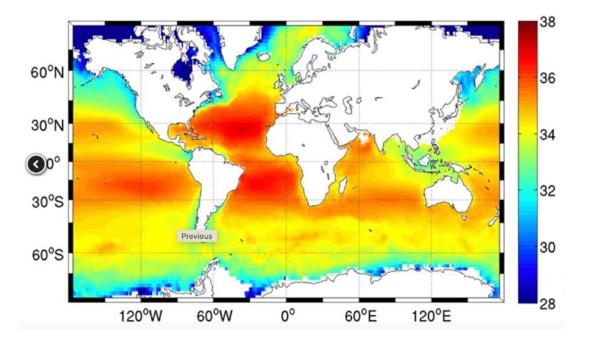
Further reaction to form magnesium bicarbonate absorbs in total of up to 2 moles of CO_2 per mole of magnesium:

$$MgCO_3 + H_2O + CO_2 \leftrightarrow Mg(HCO_3)_2$$

Due to the reversible nature of this second reaction, the ratio achieved in practice is less than 2, with an estimated in the range 1.4 to 1.7 according to conditions of CO_2 concentration, temperature, and salinity.

Compared to the Chloralkali process (House et al, 2007), which may be considered the most similar option to the current one, Davies et al (2018) calculated a **significant lowering of energy penalty, by a factor of about 1.5–5, using electrolysis-GDA**.

The electrolysis-GDA process could be applied not just to desalination brine but also to **raw seawater**. If raw seawater was used, it would be more effective to concentrate on parts of the ocean with the highest salinity. The following map shows ocean salinity world-wide. In parts per thousand.



The mid Atlantic off both north and south America have the highest **salinity**. The salinity of the brine from desalination plants averages about 80 ppm, more than double the input salinity which is usually about 35-37 ppm. Thus, the salinity of brine, while higher than that of the ocean water input, is not that much higher. If this is the cheapest electrolysis method, it needs to be investigated.

d. EW with Production of Hydrogen Gas (H₂) by Electrolysis vs BECCS

Rau et al (2018) estimated that methods of combining saline water electrolysis with mineral weathering powered by any source of non-fossil fuel-derived electricity could, on average, increase energy generation and CO₂ removal by >50 times relative to BECCS, at equivalent or lower cost. The BECCS NET is Bioenergy with Carbon Capture and Storage.

This electrogeochemistry avoids the need to produce and store concentrated CO_2 , instead converting and sequestering CO_2 as already abundant, long-lived forms of ocean alkalinity. Such energy systems could also greatly reduce land and freshwater impacts relative to BECCS and could also be integrated into conventional energy production to reduce its carbon footprint.

Rau et al (2018) evaluated the application of recently described electrogeochemical methods of converting any non-fossil fuel-derived electricity source to a negative-emissions fuel or energy carrier, H₂. This is outlined in the following figure.

Figure below. Various schemes for electrolytically generating H_2 while consuming CO_2 and transforming it to dissolved mineral bicarbonate. When powered by electricity derived from lowor non-CO₂-emitting energy sources, these schemes are strongly CO₂-emissions negative. Fig a. Scheme according to House et al, (2007). Fig b. Scheme according to refs Rau, (2008), Rau et al, (2013) . Fig c. Scheme according to Willauer, et al (2017). SW = seawater; Vd.c. , direct current electricity.

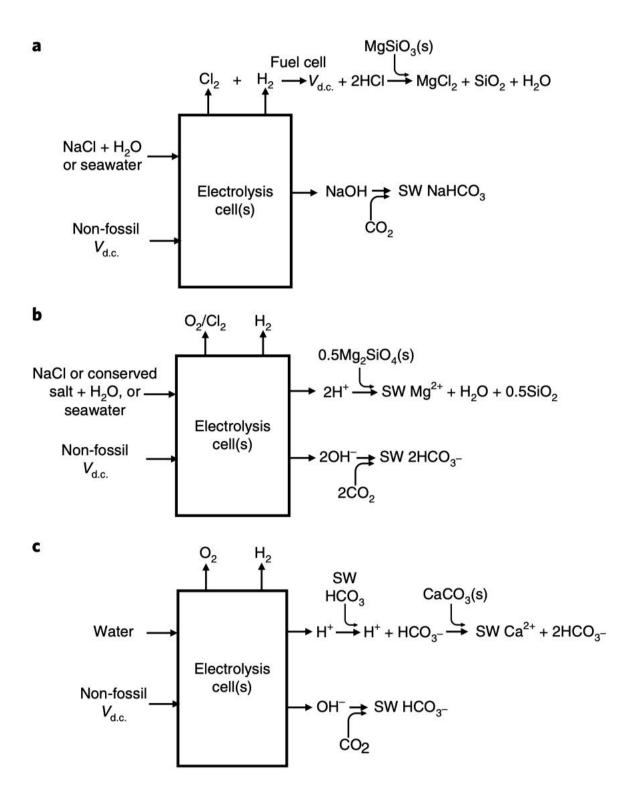


Fig a. Central to these processes is the splitting of water at a cathode to form H_2 (gas) and OH⁻, with the generation of O_2 (gas) or Cl_2 (gas) and H⁺ at the anode. In one approach (House et al, 2007) the Na⁺ + OH⁻ produced during electrolysis of a NaCl solution (**chloralkali process** – see above) is used to absorb atmospheric CO₂ and convert it to NaHCO₃ (plus, via chemical equilibrium reactions, a smaller amount of dissolved Na₂CO₃. The H₂ and Cl₂ gases generated are reacted in a fuel cell to produce electricity and HCl (acid). The HCl is subsequently neutralized with alkaline silicate minerals to produced benign Mg and Ca chlorides and silica.

Fig b. In a second approach the H^+ produced in the anolyte is directly neutralized with alkaline carbonate or silicate minerals, forcing the remaining electrolyte to accumulate OH^- , which is then used to absorb CO_2 from the atmosphere.

Fig c. A third method (Willauer, et al, 2017) employs membranes to separate the OH⁻ (alkaline) and H⁺ (acid) solutions produced in compartmentalized water electrolysis, with the latter then used to acidify seawater and thus convert a substantial portion of its resident, dissolved bicarbonate, and carbonate to dissolved CO₂ (or carbonic acid, H⁺ + HCO3⁻). This CO₂ can subsequently be degassed and sequestered from the atmosphere, or as will be explored here, converted (without degassing) to dissolved seawater bicarbonate (plus carbonate) via spontaneous reaction with solid carbonate minerals (Rau & Caldeira, 2019; Rau, 2011), thus effecting CO₂ sequestration. Simultaneously, the OH⁻ stream produced in the preceding electrolysis is also added to seawater to effect air CO₂ capture and storage as dissolved mineral (bi)carbonates in the ocean.

Rau et al (2018) calculated the energy requirements of the above three, a-c, approaches. We leave the details to the interested reader. However, they concluded that their approach is a negative-emissions energy strategy with the potential to greatly expand the global resource beyond that previously estimated for BECCS, with the added benefits of

(1) lessening or avoiding land use and land ecology impacts,

(2) increasing the quantity of CO_2 removal per unit of energy generated,

(3) avoiding the expensive production and risky storage of concentrated CO_2 inherent in CCS, and

(4) achieving these benefits at estimated costs equivalent to or lower than BECCS.

Carbon storage occurs by converting CO₂ to dissolved alkaline bicarbonates and carbonates that, when added to the already very large reservoir of these compounds in the ocean, provide long-term carbon sequestration while helping counter ocean acidification.

In contrast to the land-based approach described by Rau et al (2018), in this ship-based approach all the energy produced in the form of H₂ would be utilized onboard to provide locomotion and energy for electrolysis. What percentage of the electricity used for electrolysis can be recouped with H₂ fuel cells? And, which of the electrolysis approaches, including electrolysis GDA, is most efficient? Which is best suited to a ship-based approach? Answers to these questions are pending.

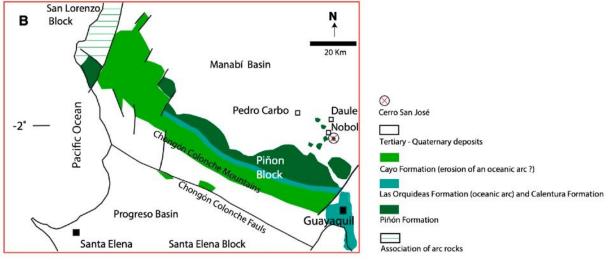
An Equatorial Project

The above review identified an equatorial region along the equator west of Ecuador with the following characteristics:

- High levels of out gassing of CO₂ from the ocean to the atmosphere that needs to be reversed.
- High levels of salinity making electrolysis more efficient.

• The availability of extensive ophiolite deposits in the nearby South American Countries (Villares et al 2020; Blanco-Quintero et al 2020; Bourgois, et al 1987; Spadea et al 1987; Kaeding, et al 1990) and New Caledonia.

There is also a deposit of ultramafic rock just north of Guayaquil, Ecuador that could supply the rocks for this project (see map). New Caledonia is also a possibility (see above).



Geological map of Ecuador of the Piñón ophiolite block north of Guayaquil.

These observations suggest an Equatorial Project in which the specialized ships described above, loading ultramafic rocks, and operating out of Guayaquil, Ecuador, could address the high rate of out gassing in this area. Such highly focused projects may be much more effective than general ocean wide alkalinization.

Protecting the Great Barrier Reef

Feng et al, (2016) concluded that OAE may be a method that could help to keep regional coral ecosystems within saturation states and pCO_2 values close to present-day values even in a high-emission scenario and thereby might 'buy some time' against the ocean acidification threat, even though regional EAO does not significantly mitigate the warming threat.

A distinct advantage of using ships as platforms for electrolysis eEAO is that the efforts can be focused on critical area such as the Great Barrier Reef.

Contribution of Rivers to OAE

Gomez et al (2021) examined ocean acidification in the Gulf of Mexico and found a significant natural contribution to ocean alkalinity from the runoff of the Mississippi River due to an increasing Mississippi river alkalinity concentration, a property related to the water capacity to neutralize acidification.

Long Term Effects of OAE.

Gonzales and Ilyina (2016) have modeled the effects of large scale OAE. The addition of 114 Pmol of alkalinity to the surface ocean stabilizes atmospheric CO₂ concentration to RCP4.5 levels under RCP8.5 emissions. To maintain atmospheric CO₂ at RCP4.5 levels under the high-emission scenario RCP8.5, $\approx 114 \cdot 10^{15}$ mol (10¹⁵ mol = 1 Pmol) of added alkalinity would be needed until the year 2100 in total. This implies an increase in the globally averaged

surface TA concentration of around 30%. To produce 114 Pmol of TA, about $4.01 \cdot 10^{12}$ metric tons (Tt or trillion t) of olivine would be needed, which would require an increase of 3 orders of magnitude in the total olivine production until 2100.

This scenario removes 940 GtC from the atmosphere and mitigates 1.5 K (or 1.5 °C) of global warming within this century. The climate adjusts to the lower CO₂ concentration preventing the loss of sea ice and high sea level rise. Seawater pH and the carbonate saturation state (Ω) rise substantially above levels of the current decade. Pronounced differences in regional sensitivities to OAE are projected, with the Arctic Ocean and tropical oceans emerging as hot spots for biogeochemical changes induced by OAE. Thus, the CO₂ mitigation potential of OAE comes at a price of an unprecedented ocean biogeochemistry perturbation with unknown ecological consequences. All in all, the effects seem positive.

Studies of OAE and eOAE

Kheshgi, (1995). Ocean alkalinity might be raised by introducing the dissolution products of alkaline minerals into the oceans. Naturally occurring soda ash (Na_2CO_3) is readily soluble and easily mined. The world's production of soda ash in 2019 was 57 million metric tons. Increasing ocean alkalinity might have the environmental benefit of chemically buffering the oceans to the increased concentration of CO₂, although there might be impacts by contaminants or local pH effects which would have to be evaluated. Increasing ocean alkalinity is a means by which CO₂ might be sequestered from the atmosphere.

Lackner (2002) has expanded on the alkalinity approach. Sequestration of waste carbon dioxide will require methods that can safely store several trillion tons of carbon dioxide. Long-term storage of a gaseous substance is fraught with uncertainty and hazards, but carbonate chemistry offers permanent solutions to the disposal problem. Carbonates can be formed from carbon dioxide and metal oxides in reactions that are thermodynamically favored and exothermic, which result in materials that can be safely and permanently kept out of the active carbon stocks in the environment. Carbonate sequestration methods require the development of an extractive minerals industry that provides the base ions for neutralizing carbonic acid.

For carbon management applications, **the most important independent variable is alkalinity** because it very directly controls the amount of stored inorganic carbon. One may want to control its value by titrating ocean water with sodium carbonate (Kheshgi, 1995) (see above). By adding alkalinity to the surface water, one could maintain a constant PCO₂ over the water. **This strategy would minimize greenhouse gas impacts by effectively removing excess carbon dioxide from the air.** Changing the alkalinity would raise the uptake capacity of the surface ocean and ultimately of the full ocean. **Any carbon management strategy that is based on increasing alkalinity could have the ocean take up 10,000 Gt of carbon** with changes in PCO₂, [CO⁻³] and [H+] that could be held below 25%. It is remarkable that these changes, which could accommodate the disposal of most of the available fossil carbon, are smaller than those that have already occurred in surface waters due the increase in PCO₂.

Controlling the alkalinity of the ocean may be motivated not so much by a desire to eliminate the climate change impact of fossil fuel consumption but by the desire to correct the chemical imbalances caused by the dissolution of carbonic acid in the world's oceans. As a by-product of maintaining the oceans' carbonate ion concentration and pH as close to constant as

possible, the increased carbon uptake capacity of the oceans would remove nearly all the excess carbon dioxide from the atmosphere and retain it on geological timescales.

The Lackner (2002) paper is very detailed. It adds some hope to the possibility that Increasing the alkalinity of the ocean in the Great Barrier Reef would help to save the reef.

Henry (2008) In regard to the use of calcium carbonate to produce alkalinization of the ocean, Harvey (2008) concluded the following: CaCO₃ could be added to the surface layer in ocean regions where the depth of the boundary between supersaturated and unsaturated water is relatively shallow (250–500 m) and where the upwelling velocity is large (30–300 mt/yr). The CaCO₃ would dissolve within a few 100 m depths below the saturation horizon, and the dissolution products would enter the mixed layer within a few years to decades, facilitating further absorption of CO₂ from the atmosphere. This absorption of CO₂ would largely offset the increase in mixed layer pH and carbonate supersaturation resulting from the upwelling of dissolved limestone powder. However, if done on a large scale, the reduction in atmospheric CO₂ due to absorption of CO₂ by the ocean would reduce the amount of CO₂ that needs to be absorbed by the mixed layer, thereby allowing a larger net increase in pH and in supersaturation in the regions receiving $CaCO_3$. At the same time, the reduction in atmospheric pCO₂ would cause outgassing of CO₂ from ocean regions not subject to addition of CaCO₃, thereby increasing the pH and supersaturation in these regions as well. Geographically optimal application of 4 billion t of CaCO₃ yr (0.48 Gt C/yr) could induce absorption of atmospheric CO₂ at a rate of 600 Mt CO₂/y after 50 years, 900 Mt CO₂/yr after 100 years, and 1050 Mt CO₂ /yr after 200 years. The time frames are daunting.

He examined the energy required to grind the limestone, the logistics of and energy use associated with dispersal by ship, and ecological impacts. The task would be enormous and would need to continue over a period of 100 years.

Hangx and Spiers (2009) The feasibility of spreading olivine on coastlines depends on the rate of olivine dissolution, the sequestration capacity of the dominant reaction, and its CO_2 footprint. Kinetics calculations show that offsetting 30% of worldwide 1990 CO_2 emissions by beach weathering means distributing of 5.0 Gt of olivine per year. For mean seawater temperatures. To obtain useful, steady state CO_2 uptake rates within 15-20 years requires a grain size of < 10 um. However, the preparation and movement of the required material poses major economic, infrastructural, and public health questions. We conclude that coastal spreading of olivine is not a viable method of CO_2 sequestration on the scale needed.

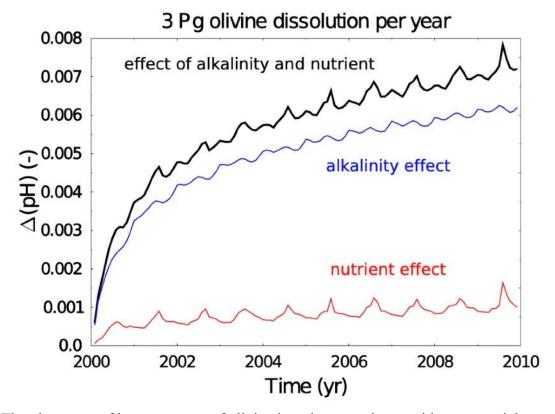
This "**Green Beaches**" proposal entails the spreading of crushed olivine rock along large parts of the Earth's coastlines, above the wave base, using coastal dumper barges and/or beach bulldozer equipment. Weathering is a slow process much skepticism exists in the scientific community regarding CO₂ sequestration by weathering approaches.

In contrast to the optimistic cheap tool of Schuiling and Krijgsman (2006), Hang and Spiers point out that with the **sand grain size of the Schuiling report it would take 370 to 6,010 years for the complete dissolution of olivine**. Dissolution is significantly accelerated with grain sizes of >10 um but achieving that small size adds considerable expense to EW. Thus, one of their conclusions is that mining, crushing, and grinding of olivine to a grain size of <10 um will reduce process efficiency by 5-11% for pure olivine and by 10-20% for typical olivine rock. This does not seem unsurmountable. An additional 0.1 to 1% efficiency reduction will be generated per 100 km of transport of one ton of crushed olivine rock by ship, train, or truck. Typical transport distances in Europe would be ~ 1000 km.

Terrestrial spreading of crushed olivine in tropical areas is more promising than beach reaction, especially on land with acidic soils. However, beach weathering could contribute perhaps a 1% equivalent reduction as a niche activity, particularly in tropical regions where reaction rates are accelerated. More research on costs, logistics and seawater reaction rates is needed to clarify the possible contribution.

Kohler et al (2013); Hauck, et al, (2014) concluded that if dissolved in the surface ocean, olivine sequesters 0.28 g carbon per g of olivine dissolved, similar to land-based enhanced weathering. Silicic acid input, a byproduct of the olivine dissolution, alters marine biology because silicate is in certain areas the limiting nutrient for diatoms. As a consequence, their model predicted a shift in phytoplankton species composition towards diatoms, altering the biological carbon pumps. Enhanced olivine dissolution, both on land and in the ocean therefore needs to be considered as ocean fertilization. From dissolution kinetics they calculate that only olivine particles with a grain size of the order of 1 μ m sink slowly enough to enable a nearly complete dissolution. The energy consumption for grinding to this small size might reduce the carbon sequestration efficiency by ~30%.

The following figures shows the effect of ocean pH of the placement of 3 Pg or 3 billion tons of olivine per year.



The placement of large amounts of olivine into the ocean is not without potential problems. Its limitations are distributing 3 Pg olivine per year: full-time commitment of more than **300 large ships. This would sequester approximately 9% of anthropogenic CO**₂

emissions. This estimate has not taken into consideration the increased efficiently of utilizing electrolysis or the use of heOAE.

Some of the risks are: Dissolution of heavy metals possible - toxicity? Impact on marine species distribution. Potential for extension of anoxic or sub-oxic regions. Environmental and social problems with mining of olivine. These are discussed in detail below.

Renforth and Henderson (2017) Assessing Ocean alkalinity for carbon

sequestration. Carbon storage in the ocean as bicarbonate ions (by increasing ocean alkalinity) has received very little attention. Seawater has a high alkalinity (2.5 mEq/kg) which, coupled to the large volume of the ocean, makes oceanic inorganic C by far the largest C reservoir in the ocean-atmosphere-biosphere system (\approx 42,000 Gt C (Ciais et al., 2014). The oceans have a sufficient capacity to sequester copious quantities of CO₂. It may be possible to sequester hundreds of billions to trillions of tons of C without surpassing postindustrial average carbonate saturation states in the surface ocean. When globally distributed, the impact of elevated alkalinity is potentially small and may help ameliorate the effects of ocean acidification. However, the local impact around addition sites may be more acute but is specific to the mineral and technology.

The alkalinity of the ocean increases naturally because of rock weathering in which >1.5 mol of carbon are removed from the atmosphere for every mole of magnesium or calcium dissolved from silicate minerals (e.g., wollastonite, olivine, and anorthite) and 0.5 mol for carbonate minerals (e.g., calcite and dolomite). These processes are responsible for naturally sequestering 0.5 billion tons of CO₂ per year. Alkalinity is reduced in the ocean through carbonate mineral precipitation, which is almost exclusively formed from biological activity.

Most of the previous work on the biological response to changes in carbonate chemistry have focused on acidifying conditions. More research is required to understand carbonate precipitation at elevated alkalinity to constrain the longevity of carbon storage. A range of technologies have been proposed to increase ocean alkalinity (accelerated weathering of limestone, enhanced weathering, electrochemical promoted weathering, and ocean liming), the cost of which may be comparable to alternative carbon sequestration proposals (e.g., \$20–100 tCO). There are still many challenges that warrant research.

The oceans contain \approx 38,000 Gt C, some 45 times more than the present atmosphere, and oceanic uptake has already consumed close to 40% of anthropogenic C emissions. So, the issue is not capacity, but rather a question of how to accelerate oceanic uptake and storage in a safe and cost-effective way. Given the increasing reliance of future climate scenarios on negative emission, and the size of C sequestration that may be required, it is important to explore and understand the feasibility of all possible C sinks, including acceleration of the natural oceanic sink. Sequestration of inorganic C in the ocean is the least represented climate mitigation strategies in the literature (Bellamy et al., 2012).

Alkalinity storage in the ocean raises issues around environmental impact, quantification, monitoring, governance, and longevity, all of which were explored in detail in this review. (see below).

Storage of C by increasing ocean alkalinity requires the extraction, processing, and dissolution of minerals. This results in chemical transformation of CO_2 and sequestration as bicarbonate and carbonate ions (HCO_3^{-1} and CO_3^{2+}) in the ocean. Dissolution of a mole of Ca^{2+} or Mg²⁺ sequesters close to 2 mol of C. Examination of several natural minerals showed that **olivine (forsterite) Mg_2SiO_4 was the most efficient in terms of grams CO_2 sequestered per**

gram of mineral (1.25). This compared to magnesite MgCO₃ (0.52), Calcite CaCO₃ (0.44), Dolomite CaMg(CO₃)₂ (0.48) and anorthite CaAl₂Si₂O₈ (0.32). The gCO₂/g mineral is higher for man-processed minerals. These include Lime CaO (1.57), Portlandite Ca(OH)₂ (1.19), Periclase MgO (2.18), and Brucite Mg(OH)₂ (1.51). However, these would not be available in very large quantities. (but see Fakhraee 2023 below).

As shown previously, on land olivine, CO₂ and water produce magnesium carbonate:

 $Mg_2SiO_4 + 2CO_2 + 2H_2O \rightarrow 2MgCO_3 + H_4SiO_4$

If the cations (Mg⁺⁺, Ca⁺⁺) are transported to the ocean, they increase the alkalinity (see above - alkalinity) and lead to transfer of CO_2 to HCO_3^- and CO_3^{2-} . The resulting decrease of dissolved CO_2 causes uptake of atmospheric CO_2 by air-sea gas exchange.

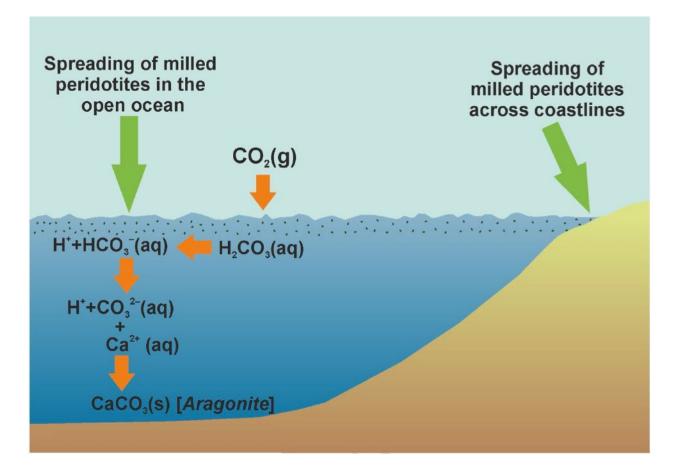
Addition of sufficient Ca^{2+} to fully compensate for present anthropogenic emission of 10 Gt C/yr requires addition of 20 Gt Ca^{2+} /yr. This is ≈ 20 times the annual riverine input of Ca^{2+} , a very significant perturbation, and obviously a very substantial undertaking in engineering terms. The large volume of the ocean and its high Ca^{2+} concentration, however, mean that the oceanic perturbation is very much smaller and only a 0.9 mmol kg/yr increase in Ca^{2+} is required. Even if considering the surface ocean alone this annual addition is less than a 0.3% increase in total Ca^{2+} .

Rayner et al. (2013) have laid out a set of guiding ("Oxford") principles for geoengineering, including (1) that it be regulated as a public good, (2) public participation in decision-making, (3) disclosure of research and open publication of results, (4) independent assessment of impacts, and (5) governance before deployment.

Griffioen (2017) examined the effect of Fe rich versus Mg rich olivine. They concluded the efficiency of olivine weathering depended on the Mg/Fe fractions of olivine and precipitation of secondary minerals. For Fe-rich olivine, CO_2 may be released to the atmosphere and ocean pH might decrease during oxic olivine weathering. Ocean alkalinization only happens when more than 1 mol/kg H₂O Mg-rich olivine weathers. The abundance of Mg compared to Fe depends on the rock but is about 90% in the most abundant dunite.

Maintenance of supersaturation for calcite or aragonite in seawater reduces the efficiency by about a factor of two compared to the efficiency without secondary precipitation. Precipitation of sepiolite as Mg silicate reduces the efficiency even more.

Rigopoulos et al (2017) The following figure is from Rigopoulos et al: (2017) Carbon sequestration via enhanced weathering of peridotites and basalts in seawater.



This study was designed to assess the potential drawdown of CO_2 directly from the atmosphere by the enhanced weathering of peridotites and basalts in seawater. Experimentally measured dissolution rates by Wolff-Boenisch et al. (2011) suggested that ground ultramafic rocks could lead to the efficient carbon dioxide mineralization in seawater.

In the Rigopoulos et al (2017) study, pulverized, and ball-milled dunite, harzburgite and olivine basalt were reacted in artificial seawater in batch reactor systems open to the atmosphere for two months. The results demonstrate that the **ball-milled dunite and harzburgite changed dramatically the chemical composition of the seawater within a few hours, inducing CO₂ drawdown directly from the atmosphere and ultimately the precipitation of aragonite (see above figure). In contrast, pulverized but un-milled rocks, and the ball-milled basalt, did not yield any significant changes in seawater composition during the two-month experiments.**

Zhang et al (1997) reported that ball mill results in a structural change from a crystalline state into an amorphous one. This change is attributed to local disordering around magnesium in the structure. This disordering leads to enhancement of extraction of both magnesium and silicon from the mechanically activated serpentine by the acid solutions. Concentrations of both elements in the mother solutions increase with an increase in grinding time.

These results demonstrate that **ball-milling can substantially enhance the weathering** rate of peridotites in marine environments, promoting the permanent storage of CO_2 as environmentally benign carbonate minerals through enhanced weathering. The

precipitation of Mg-silicate clay minerals, however, could reduce the efficiency of this carbon sequestration approach over longer timescales.

What is ball-milling?

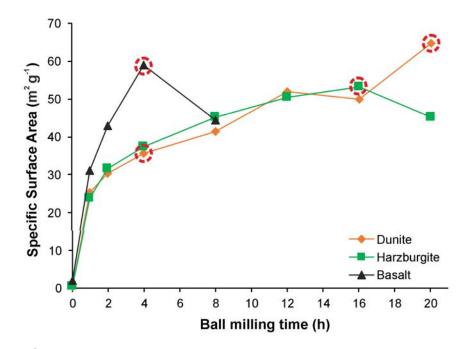


A **ball mill** or **roller mill** is a type of grinder used to grind or blend materials for use in paints, pyrotechnics, ceramics, and selective laser sintering. It works on the principle of impact and attrition: size reduction is done by impact as the balls drop from near the top of the shell. The process of grinding is called **comminution**.

A ball mill consists of a hollow cylindrical shell rotating about its axis. The axis of the shell may be either horizontal or at a small angle to the horizontal. The grinding media are the balls, which may be made of steel (chrome steel), stainless steel, ceramic, or rubber. The inner surface of the cylindrical shell is usually lined with an abrasion-resistant material such as manganese steel or rubber lining. Less wear takes place in rubber lined mills.

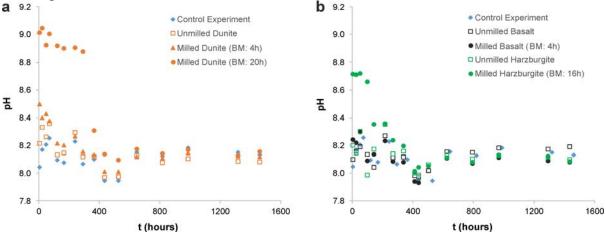
Fuerstenau, and Abouzeid (2002) examined the relative cost of different machines and other factors. The required energy for comminution is proportional to the new surface produced. Efficiencies for the most used mills ranged from 7–32%. In some cases, the efficiencies are as low as .15%. The wet grinding in tumbling mills is more efficient than the dry grinding. One reason for this is that water is adsorbed on the newly created surfaces and prevents the fines from agglomerating. The second reason is that the fine particles produced during comminution remain suspended in the aqueous medium, thereby increasing the chance for the coarser particles to be broken by the tumbling media.

The effect of various times in the ball-mill was measured by the BET method (adsorption of N_2 at 77 K) and was carried out in a Micromeritics Gemini III Surface Area and Pore size Analyzer to determine the specific surface area (m²/g).



BET (m^2/g) specific surface area versus ball milling time for the studied rock materials (red circles show the milled samples used during the experiments). The BET values for the milled basalt and dunite samples were acquired from Rigopoulos et al. (2015) and Rigopoulos et al. (2016), respectively.

This showed that it takes about 12 hours to grind these rocks to a size that maximizes the desired effect. The following figure shows that in seawater, milled dunite (a) and milled Harzburgite (b) show a pH of 8.7 to 9.0. Milled basalt and the controls showed a pH of 8.0 to 8.2. This is the pH range of natural seawater (Marion et al., 2011). This supports other studies showing the ineffectiveness of basalt.



Temporal evolution of the reactive fluid pH: (a) Control experiment, and experiments with unmilled and milled dunite; (b) Control experiment, and experiments with unmilled and milled basalt and harzburgite.

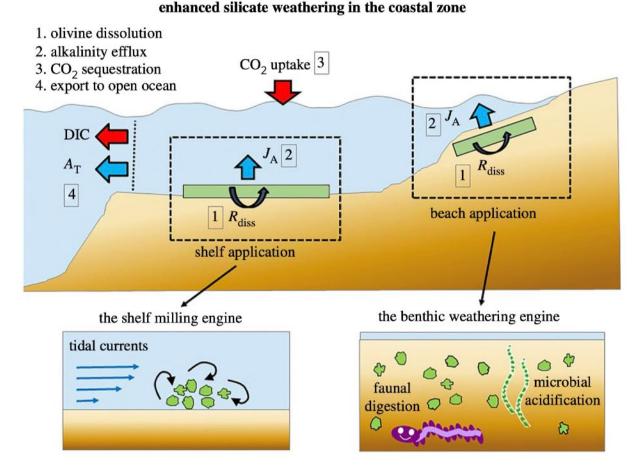
This indicated that only the 20-hr milled dunite (olivine) showed an increase in alkalinity to pH 9.0 starting after 6 hours. After several hundred hours the pH decreased back to @ 8.2. These experiments provide information as to the relative effect of these three milled minerals, dunite, harzburgite and basalt, in combating ocean acidification. Dunite was most effective, harzburgite next most, and basalt was ineffective. The conclusions were:

- Peridotites (olivine and mafic pyroxene) induced CO₂ drawdown directly from the atmosphere via mineralization.
- The basalt did not yield any significant changes in seawater composition.
- The precipitation of sepiolite could reduce the carbon sequestration efficiency.

Many more details about the best machines to produce fine and ultra-fine particles by milling are given in **Appendix G Final Stage Grinders** (see web site).

So, what is sepiolite? It is also known as meerschaum, is a soft white clay mineral, often used to make tobacco pipes (known as meerschaum pipes). It is a complex magnesium silicate, a typical chemical formula for which is $Mg_4Si_6O_{15}(OH)_2 \cdot 6H_2O$, it can be present in fibrous, fine-particulate, and solid forms. Only small amounts of it were formed in the grinding process.

Meysman and Montserrat, (2017) These authors discuss the potential of applying EW in coastal environments, both beaches and shelf, as a climate change mitigation option. By deliberately introducing fast-weathering silicate minerals onto coastal sediments, alkalinity is released into the overlying waters, thus creating a coastal CO₂ sink. Compared with other NETs, **coastal EW has the advantage that it counteracts ocean acidification, does not interfere with terrestrial land use, and can be directly integrated into existing coastal management programmer with existing (dredging) technology.**



Two **ESW** (Enhanced Silicate Weathering) application scenarios have been proposed: (a) spreading coarse particles into high-dynamic shelf environments where particles are crushed during bedload transport ('shelf milling') and (b) spreading finer olivine sand onto beaches and shallows, where dissolution is enhanced through biotic processes in the seabed ('benthic weathering engine').

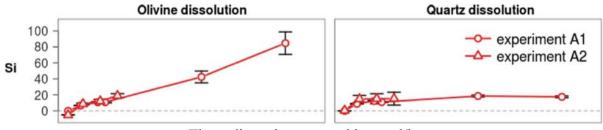
The seabed is characterized by various forms of biological activity, which could induce higher dissolution rates compared with sterile laboratory conditions. Such biological enhancement of silicate weathering has been extensively documented in **terrestrial soils**, giving rise to the '**mycorrhizal weathering engine' concept where both microorganisms and invertebrate fauna act as agents of enhanced weathering in marine sediments**. Together, the interplay of microbial metabolism and macrofaunal bioturbation could substantially increase the rate of olivine dissolution under in situ conditions.

Dedicated experiments are needed (i) to determine the weathering rate more precisely under in situ conditions within the seabed and (ii) to evaluate the ecosystem impacts—both positive and negative—from the released weathering products.

Montserrat, F. et al (2017) These authors specifically address several questions related to the application of enhanced silicate weathering (ESW) in natural coastal environments: (1) What is the rate of olivine dissolution in natural seawater and how does this differ from artificial seawater? (2) Does olivine dissolve stoichiometrically in natural seawater? (3) What dissolution

products can be used to efficiently monitor the dissolution rate of olivine in coastal sediments, i.e., quantify the efficiency of enhanced silicate weathering? (4) To what extent does secondary mineral formation diminish the CO_2 sequestration efficiency of olivine dissolution in seawater?

Commercially available olivine sand (Mg^2-xFe^x SiO4) and lab-grade quartz (SiO₂) were used in slurry dissolution experiments. The olivine sand (particle size quantiles: D10 = 91 µm, D50 = 143 µm, D90 = 224 µm) had a molar Mg-to-Fe ratio of 0.94:0.06, characterizing the olivine as forsterite-94 (Fo₉₄). The Ni content was estimated at 0.0075 mol Ni/mol olivine. The olivine or quartz were placed as a slurry of into borosilicate glass bottles and placed on a rotating shaking platform. The fluids were filtered seawater (FSW), artificial seawater (AFW) with or without Ca or Mg. The following figure shows the rate of silicon release over a **period of 100 days for olivine and quartz.**



The ordinate is measured in umol/kg

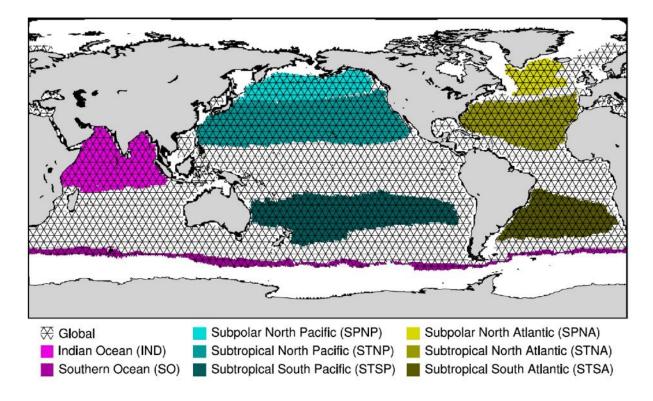
The main results of forsterite olivine dissolution in the ocean are increases in Mg^{2+} , Si, TA (total alkalinity), DIC (dissolved inorganic carbon), Fe⁺², and Ni⁺². Their effects on the ecosystem effects need to be assessed.

While increases in alkalinity and DIC are a desired effect for climate engineering purposes, the increase in Mg^{+2} is not expected to pose a significant threat because of the high background concentration in seawater. Increases in dissolved Si and dissolved Fe can stimulate primary production and thus lead to additional CO₂ sequestration, as recently assessed by model analysis. However, the ultimate impacts on coastal food webs of fertilizing by olivine dissolution are uncertain and need further investigation.

Lenton et. al. (2018) reported on simulation of adding olivine to costal seawater and concluded that it could sequester 524-676 Gt of CO₂ between 2020 and 2100* equivalent to a rate of 5.55 to 8.45 Gt per year. The simulations of Feng et al (2017) suggested the figure could be as high as 971 Gt CO₂ sequestered at the same time, equivalent to a rate of 12.1 Gt per year. (• as reported by Coba et al, 2022).

Additional Ventures (2022) is a well-funded nonprofit formed by Mike Schroepfer, Meta's former Chief Technology Officer. It is dedicated to accelerating research into ocean alkalinity enhancement. There is an excellent review of OAE on its website entitled **Ocean Alkalinity Enhancement R&D Program**. In addition to the R & D, they propose to develop meaningful frameworks for monitoring, reporting and verification (MRV). Any MRV framework will have to focus on two major questions. First, how much CO₂ is permanently moved from the atmosphere to the ocean and how quickly does this happen (carbon accounting)? Second, what are the undesired effects of OAE on marine organisms and ecosystems (monitoring of environmental impacts) and how can they be mitigated? This document also lists other organizations that have taken up the cause of ocean based CDR. They describe OAE in the following terms. When alkalinity increases in seawater, dissolved CO_2 is chemically transformed to bicarbonate and carbonate ions. This transformation can help de-acidify seawater. OAE can, at least on paper, sequester billions of tons of CO_2 annually for tens or even hundreds of thousands of years.

Burt, D. J. et al (2021) Based on computer simulations the authors concluded that the regional implementation of OAE can sequester more atmospheric CO_2 than a global implementation. The eight regional areas (gyres) they proposed are shown in the following diagram.



The Subpolar North Atlantic displayed a previously unexpected alkalinity sensitivity increase in response to high total alkalinity concentrations. It sequestered 12% more carbon than the Global experiment despite OAE being applied across a surface area 40 times smaller. The simulations covered a 75-time span. Carbon uptake of regionally deployed OAE ranged between 82 and 175 PgC compared to the Global, where 157 PgC was sequestered. This range of carbon uptake illustrated the effect regional variation of a number of factors such as background DIC, TA and temperature. The alkalinity input subroutine was based on that of González and Ilyina (2016). In the idealized ocean-only set-up, TA was enhanced at a rate of 0.25 Pmol/year.

NAS (2022) OAE Chapter 7 Alkalinity Enhancement of the National Academies of Science, Engineering and Medicine document entitled A Research Strategy for Ocean-based Carbon Dioxide Removal and Sequestration. Washington, DC: The National Academies Press. provides a thorough 26-page review of OAE.

When large amounts of pulverized silicate or carbonate rock or their dissolution products are added to the ocean it adds alkalinity to the surface ocean and thereby "locks" CO_2 into other forms of dissolved inorganic carbon (DIC), which is expected to promote atmospheric CO_2 influx into the ocean. Specifically, following alkalinity addition, CO_2 is converted into bicarbonate ions (HCO^{3-}) and carbonate ions (CO_3^{2-}), and these chemical changes lead to a rise in pH.

They conclude that research is needed to assess the ecological response to OAE. Although much can still be learned from laboratory-based and mesocosm experiments, including exploring the impacts of OAE on the physiology and functionality of organisms and communities, implementation pathways to responsible deployment will require **field trials**. Such trials will be essential to assess how sunlight zone and ocean floor biogeochemical processes are affected, and the response from complex communities.

Hartmann, J. et al (2022, 2023) state that one of the concerns about OAE is the stability of alkalinity when added to seawater. Seawater is already supersaturated with respect to calcium carbonate minerals, and an increase in total alkalinity together with a corresponding shift in carbonate chemistry towards higher carbonate ion concentrations would result in further increase in supersaturation, and potentially to solid carbonate precipitation. Precipitation of carbonate minerals consumes alkalinity and increases dissolved CO₂ in seawater, thereby reducing the efficiency of OAE for CO₂ removal.

A set of six experiments was performed using natural seawater with alkalinity of around 2,400 μ mol/kgw. This showed that using alkaline solutions equilibrated with atmospheric CO₂ no TA loss was observed after 4 days. In contrast, application of a solution with elevated alkalinity not equilibrated with atmospheric CO₂ caused a sustained loss of alkalinity at the first day. These results indicate that the application of CO₂-equilibrated alkaline solution bears the lowest risk of losing alkalinity due to carbonate formation if added total alkalinity (Δ TA) is less than 2,400 μ mol/kgw.

Fuhr, et al (2022) In an article entitled Kinetics of Olivine Weathering in Seawater: An Experimental Study the authors added a new twist by examining ultramafic olivine sand reacted in artificial sea water at normal atmospheric pressure and ambient temperature of 21.5–23.9°C for 134 days. The experiments were carried out in 250 ml polyethylene batch reactors. Instead of observing the expected increase in alkalinity, the alkalinity decreased over the course of the experiment. They attributed this to "the removal via precipitation of cation-rich authigenic phases that exceeded the production of the alkalinity induced by olivine dissolution." Authigenic refers to minerals that are formed in sediment or sedimentary rock. Authigenic minerals precipitate from overlying water columns. This study was caried out at the GEOMAR Helmholtz Center for Ocean Research in Kiel, Germany.

While other studies (see above) showed an increase in alkalinity from placing ground olivine in seawater, the Fuhr studies differed in that instead of using pure olivine they used a source that was 75% olivine. The rationale for this was the assumption that if OAE is to be done at scale, the amount of pure olivine is limited, and less pure sources will have to be used. This and other factors **reduced the amount of carbon removed by a factor of five** compared with olivine's theoretical potential.

In addition, the diameter of the olivine particles averaged 100 to 125 ums, significantly larger than the 1um diameter particles frequently discussed in this presentation.

Fuhr et al commented that this form of OAE may work well only in certain places where the ocean chemistry is right. That could include areas where the waters are low in salinity but rich with organic sediments, which will increase acidity.

Attention was drawn to this paper in MIT Technology Review by a note stating "Why using the oceans to suck up CO₂ might not be as easy as hoped. New studies suggest simply adding minerals or growing seaweed might be limited or costly ways of removing carbon dioxide" (Temple, 2022). However, this article concluded that these "new studies haven't delivered the final, definitive word on whether any of these methods will be feasible ways of helping to reach those carbon removal targets." Temple quoted Maria-Elena Vorrath, of the Alfred Wegener Institute for Polar and Marine Research, that the study shows the olivine process doesn't work the way we assumed. But she stressed that the mineral remains "one of the most permanent and promising methods [of CDR] nature gives us." She stated that "water mixing and other variables in the actual oceans could alter results seen in the lab."

It is notable that several companies, such as **Project Vista**, **Ebb Carbon**, **Planetary Technologies**, and **Sea Change** have sufficient faith in OAE that they are planning to use it forprofit business model to sell carbon credits.

Also of note, a National Academies panel called for setting up a \$125 million US research program to study whether we could develop ways to scale up or accelerate these processes, identify environmental side effects, and figure out how to reliably measure and verify whether carbon removal is occurring.

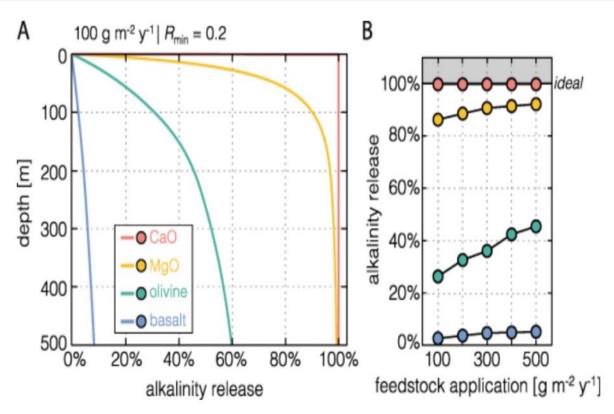
Gentile, et al (2022) reviewed the use of aircraft to disperse slacked lime (CaOH₂) for OAE. Not surprisingly, despite its effectiveness, the energy penalty and costs were much higher than distribution in the ships' wake. Although very high dispersion is reached, effects on surface microlayer were unclear. The high CO_2 emissions of the Landing to Take-Off Cycle (LTO) of the aircraft and their limited payload led to a significant CO_2 penalty, ranging between 28% and 77% of the CO_2 removal potential. Very fast discharge could reduce the penalty to 11% - 32%.

Voosen, (2022). Ocean Liming. In May, at the Apalachicola National Estuarine Research Reserve, researchers lead by Wade McGillis, at the University of Notre Dame, injected some 2000 liters of seawater enriched with lime, Ca(OH)₂, an alkaline powder and a primary ingredient in cement that's derived from chalk or limestone. The lime lowered sea level CO₂ levels by 70 ppm, allowing the water to take up more CO₂. They also monitored oyster and microbial metabolisms during the trial and saw no negative issues.

Wang H et al, (2023) simulated the climate mitigation impacts of adding alkalinity (equivalent to 667,950 metric tons NaOH/yr) in Unimak Pass on the southern boundary of the Bering Sea. They found that adding alkalinity could accelerate the ocean CO₂ uptake and storage and mitigate ocean acidification near the site of alkalinity addition. It took about 3.6 months for the ocean alkalinity enhancement impacted area to take up the extra CO₂. The cold and carbon rich water in the Bering Sea and the tendency of Bering Sea surface waters to linger near the ocean surface without mixing into the subsurface ocean both lead to high CDR efficiencies of >96%. However, even with this high efficiency, it would take >8,000 alkalinity additions of the kind we simulated to be operating by the year 2100 to meet the target to stabilize global temperatures within the targeted range.

Fakhrace et al (2022, 2023) Some sobering data on OAE. Based on a series of biogeochemical models, alkalinity sources—basalt and olivine—lead to very low CDR efficiency while strongly perturbing marine food quality and fecal pellet production by marine zooplankton. Artificial alkalinity sources—the synthetic metal oxides MgO and CaO—are potentially capable of significant CDR with reduced environmental impact, but their deployment at scale faces major challenges associated with substrate limitation and process CO₂ emissions during feedstock production.

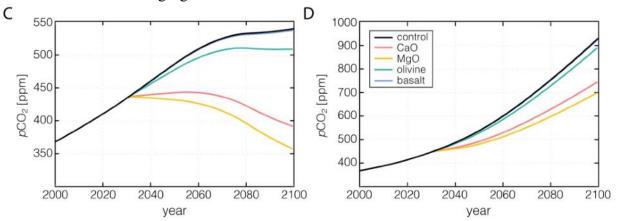
The minimal effect of olivine and basalt versus CaO and MgO is shown in the following figures.



Water column alkalinity release from solid feedstocks in the particle model. (A) Relative alkalinity release (which fosters carbon capture) as a function of depth for natural basalt, olivine, magnesium oxide (MgO), and calcium oxide (CaO). Results are shown for an idealized coastal marine ecosystem with a feedstock application rate of 100 gC/ m^2/y and a ratio between feedstock application rate and net primary productivity (R min) of 0.2 (g/g). (B) Depth-integrated efficiency of alkalinity release in the upper 80 m as a function of feedstock application rate. The grey shaded box denotes ideal (complete) alkalinity release in the surface ocean. From Fakhraee et al (2023).

This illustrates the dramatic difference in alkalinity release for basalt and olivine versus CaCO and MgO. Olivine ranged from 24 to 44 percent at different loadings. The alkalinity release for basalt was negligible. By contrast the alkalinity release for CaO was 100 percent and for MgO it ranged from 84 to 90+ percent. The effectiveness of basalt for OAE has already been ruled out (page 186).

A critical issue is the relative effectiveness at removing CO_2 from the atmosphere. This is illustrated in the following figure.

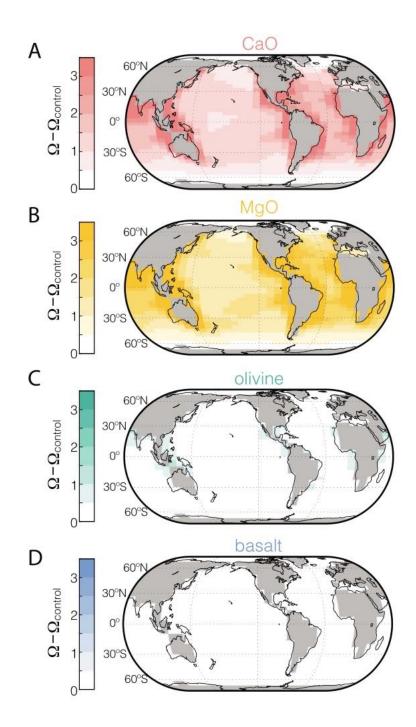


Results are shown for a moderate-emissions pathway **RCP4.5** C, and a high-emissions pathway **RCP8.5** D), with feedstock application along coastlines between 60 \circ N/S latitude. Ocean alkalinity enhancement begins in year 2030. computed as the difference in air-sea CO₂ flux relative to a control simulation with no alkalinity addition. Values are grouped according to feedstock application of (500 g/m²/y. From Fakhraee et al (2023).

With robust emissions reduction, RCP4.5, CaO and MgO were quite effective by the end of the century. With poor emissions reduction, RCP8.5 even CaO and MgO were totally ineffective. This clearly shows that using <u>NETs that remove CO₂ from the atmosphere are absolutely no excuse for not reducing emissions. A significant reduction in emissions (RCP4.5) is critical for the success of NETs.</u>

The authors also examined the estimated values of zooplankton fecal pellet production within the upper 200 m of the water column compared to those of a control simulation with no feedstock addition. Zooplankton fecal pellet production is a measure of the health of zooplankton. This showed that the use of basalt and olivine resulted in a dramatic reduction in zooplankton fecal pellet production while CaO and MgO had virtually no effect.

Finally, the authors also estimated the effectiveness of the four compounds at producing **elevated omega values throughout the oceans**, by the end of the century from 0 to 3. Omega describes the **level of calcium carbonate saturation in seawater** (see page 41).



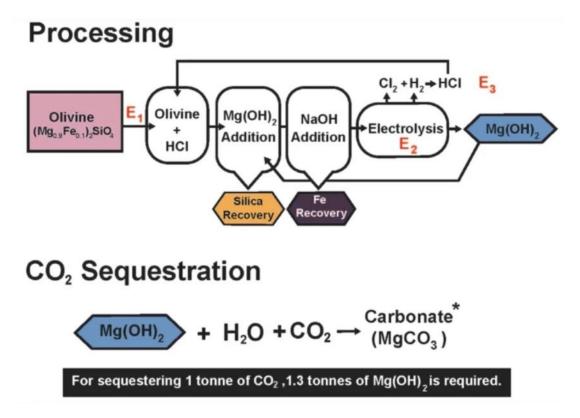
End-of-century (2100) carbonate saturation states during ocean alkalinity enhancement in an Earth system model. (A)–(D) In-situ surface ocean carbonate (aragonite) saturation states relative to a control simulation (Ω - Ω control) under a moderate emissions scenario (RCP4.5) with our benchmark feedstock application rate of 300 g m²/y along coastlines between 60° N/S latitude (see supplementary information). From Fakhraee et al (2023).

It is clear the CaO and MgO would be effective while basalt and olivine would not be effective. While they noted that obtaining such artificial compounds are scale would be a

challenge, there is a natural mineral, brucite $Mg(OH)_2$, could be utilized, *but it is much less common than olivine*. CaO and Mg(OH) could also be obtained from tailings. As outline below $Mg(OH)_2$ can also be derived from olivine.

In conclusion their results provided strong impetus for continued techno-economic assessments of novel pathways toward alkaline metal oxide production and the development of favorable life cycles for CaO and MgO deployment (Scott A et al 2021), along with **a renewed focus on electrochemical** (Rau (2008, 2029) and **reactor-based** (Rau et al, 2007) **approaches toward ocean alkalinity enhancement** that may be able to circumvent or minimize the potential deleterious ecological impacts and logistical barriers to scale that exist for olivine-based alkalinity sources. It should also be noted that the authors did not assess the use of olivine ground to 1 um size (see discussion above).

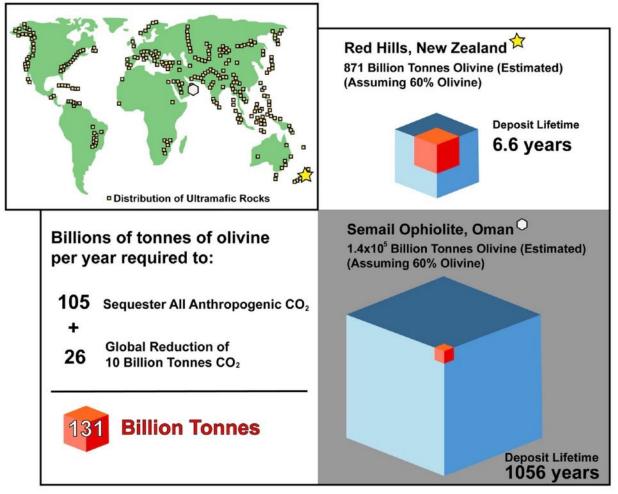
Scott et al (2021). One of the most promising materials for carbon mineralization is $Mg(OH)_2$ which, as shown above, is highly reactive and capable of forming stable carbonates. The authors describe a novel low-carbon method of **producing Mg(OH)_2**, from globally abundant olivine-rich silicate rocks. A combination of acid digestion and electrolysis of olivine were used to produce $Mg(OH)_2$ in a fully recoverable system. A total of 35 g of $Mg(OH)_2$ was produced from 100 g of olivine. The use of $Mg(OH)_2$ from olivine provides a viable pathway for significant industrial scale reductions in global anthropogenic greenhouse gas emissions. The technique is as follows.



The authors extracted $Mg(OH)_2$ directly from olivine using a combination of acid digestion and electrolysis. The acid used in the digestion process is completely recoverable and provided a source of usable energy. A slurry of recovered $Mg(OH)_2$ and water was shown to

effectively sequester CO_2 forming a hydrated Mg-carbonate. In addition to $Mg(OH)_2$, amorphous silica, has the potential for use as a partial cement replacement, was also recovered from the olivine. Since this approach also uses electrolysis, the use of renewable energy would be critical.

Ultramafic rocks, enriched in olivine, constitute ~1% of Earth's terrestrial landscape, a high proportion of oceanic crust, and >50 % of the upper mantle. As shown in the following figure, olivine-rich deposits are primarily present within populated areas of the Circum-Pacific and Mediterranean regions. The following diagram estimates the amount of olivine needed to sequester all anthropomorphic CO₂.



The general distribution of ultramafic rocks (including peridotites and serpentinites) is shown worldwide. Note that more ultramafic rock deposits are present than shown and that the squares do not represent particular sites.

La Plante et al (2021) sCS² Single-step Carbon Sequestration and Storage

La Plante et al (2021) describe what they term single-step carbon sequestration and storage or sCS^2 which relies on electrolytic carbonate mineral precipitation using renewable energy within a simple and scalable process. They cite the following unique advantages of this electrochemical technique.

1. **CO₂ mineralization occurs by producing solid carbonates**. The thermodynamic and kinetic barriers to carbonate precipitation are overcome by direct and *in situ* electrochemical

forcing to stabilize dissolved inorganic carbon and use of divalent cations, Ca⁺⁺ and Mg⁺⁺, to form carbonate minerals.

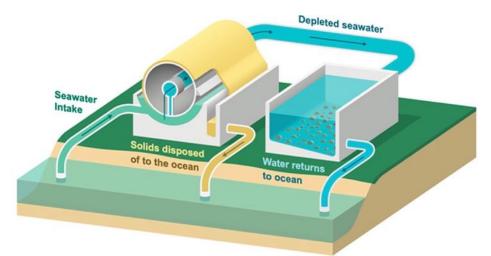
2. It utilizes flow-through electrolysis without membranes. A flowing electrolyte consisting of seawater is dissociated while in motion. Instead of membranes it utilizes cost-effective mesh electrodes with a decreasing the number of components and assembly steps thus reducing the risk of failure.

3. A rotary drum filter is used as the reactor. An electroactive thin-film mesh cathode (eTFC) is integrated within a rotary drum filter configuration. This allows for the filtration of dilute and polydisperse mineral precipitates at a low energy cost. These attributes render sCS² as worthy development, further evaluation, and scaling for global-scale carbon management.

4. The single step approach is more energy efficient than DACS. The relevant equations are:

 $CO_{2}(g) \leftrightarrows CO_{2}(aq)$ $CO_{2}(aq) + H2O \leftrightarrows H_{2}CO_{3}$ $H_{2}CO_{3} \leftrightarrows H^{+} + HCO_{3}^{-}$ $HCO_{3}^{-} \leftrightarrows H^{+} + CO_{3}^{2-}$ $Ca_{2}^{++}CO_{3}^{2-} \leftrightarrows CaCO_{3}(aq)$ $CaCO_{3}(aq) \leftrightarrows CaCO_{3}(s)$

The following diagram illustrates the general layout of sCS².



Conceptual illustration of the sCS^2 process for achieving CO^2 mineralization and disposal that utilizes an electrolytic flow reactor and integrated rotary drum filter concept to achieve rapid carbonate mineralization.

These units use 1,500 MWe/660 tons of CO_2/hr . or **2.27 MW Electrical/ton/hr**. They point out that as with Enhanced Weathering, the captured CO_2 is stored above ground or in the ocean **avoiding the potential dangers of massive underground storage**.

The basis of the sCS^2 strategy involves forcing the rapid precipitation, electrolytically, of calcium carbonate (CaCO₃), magnesium carbonate (MgCO₃), hydroxy-carbonates, and their variants by combining dissolved CO₂. For context, modern oceans are oversaturated with respect to CaCO₃, and MgCO₃ by a factor of more than 2 times. (Millero et al 2008). So, what happens to the carbonates produced? In modern oceans, calcite, and aragonite, which are polymorphs of calcium carbonate, are produced by coccolithophores (single-celled algae which form calcareous plates), foraminifera (single-celled protists), mollusks, echinoderms, and corals.

Hydrogen production and fuel cells. For every 220 metric tons of seawater that is processed, about 1 metric ton of CO₂ is removed, while simultaneously producing about **35 kilograms of hydrogen.** Thus, an additional cost-savings can come from **using the hydrogen produced in hydrogen fuel cells.** Using a fuel cell, **1 kg of hydrogen can produce 33 kWh of electricity.** Thus, for **every ton on CO₂ removed the hydrogen produced can produce 33 kW x 35 or about 1.15 megawatt of electricity.** It requires 2.27 MWe to produce 1 ton of sequestered CO₂. This suggests that **1.15/2.27 or 50% of the energy required to produce 1 ton of sequestered CO₂ can be recouped with hydrogen fuel cells. If these figures are correct, it would help immensely to reduce the total electrical energy required for this form of CO₂ sequestration.**

Alternatively, the hydrogen produced can be sold at 2-3 per kg H₂. Mineralizing 1 ton of CO₂ will produce, at minimum, 2 tons of carbonates and require 350 tons of seawater. Many other cost considerations were reviewed by the authors.

"The energy requirements of electrolytic mineralization-based CO₂ removal are **formidable**." It would be necessary to buildout 1760 plants at this scale, around the world, each having **8,410 mesh-electrode units**, to annually mineralize 10 Gt of CO₂, while consuming more than 20 PWh of electricity.

Thus, operating at scale would be expensive. The authors conclude that a massive buildout of plants would be needed, globally, incurring trillions of dollars of expenditure to achieve the required water processing throughputs and carbon mitigation scale that is required to limit global warming to the 1.5 °C threshold.

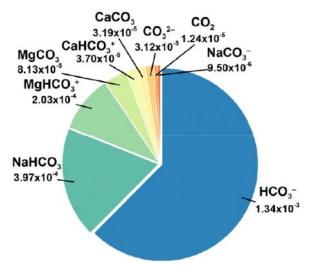
Carbon-free electricity needs to be used for this to achieve widespread viability. Ideally this could be supplied by super safe molten salt reactors (page 74).

La Plante, E. et al (2023) described the process they reported on in 2021 as the application of an electric overpotential that splits water to form H⁺ and OH⁻ ions, producing acidity and alkalinity, in addition to gaseous coproducts, at the anode and cathode, respectively. The alkalinity that results, via the "continuous electrolytic pH pump" results in the instantaneous precipitation of calcium carbonate (CaCO₃), hydrated magnesium carbonates, MgCO₃.3H₂O, hydromagnesite: Mg₅(CO₃)₄(OH)₂.4H₂O, etc.), and/or magnesium hydroxide (Mg(OH)₂) depending on the CO₃²⁻ ion-activity in solution. This results in the removal of ~4.6 kg of CO₂ per m³ of seawater catholyte processed. They also assessed changes in seawater chemistry resulting from Mg(OH)₂ dissolution with emphasis on the change in seawater alkalinity and saturation state.

The composition of seawater at 25° C and pCO₂ of =3.38 atm is as follows:

Phase	Composition
Aragonite	CaCO ₃
Artinite	$\begin{array}{c} Mg_2CO_3(OH)_2 \cdot \\ 6H_2O \end{array}$
Brucite	$Mg(OH)_2$
Calcite	CaCO ₃
Dolomite	$CaMg(CO_3)_2$
Huntite	$CaMg_3(CO_3)_4$
Hydromagnesite	$\begin{array}{c} Mg_5(CO_3)_4(OH)_2 \\ 4H_2O \end{array}$
Lansfordite	MgCO ₃ ·5H ₂ O
Magnesite	MgCO ₃
Nesquehonite	MgCO ₃ ·3H ₂ O

The relative amounts of these chemical in sea water in mol/kg is as follows:



The relative amounts for the most common ions are:

Species	Molality (<i>m</i> , mol/kg)based on Reference Composition ²⁰
Na^+	0.4860597
Mg ²⁺	0.0547421
Ca ²⁺	0.0106568
K ⁺	0.0105797
Sr^{2+}	0.0000940
Cl^{-}	0.5657647

Seawater is supersaturated with respect to aragonite, calcite, dolomite, and magnesite and undersaturated with respect to the hydrated magnesium carbonates and brucite. The CO_2 content (i.e., storage capacity) of seawater is dependent on its alkalinity. The concentration of $H_2CO_3 =$

 $K_{Hp}CO_2$ (Henry's Law) where K_{H} in seawater is 0.02858 and the partial pressure of CO_2 is 0.00042.

The Electrolytic Carbon Removal process known as the Equatic process consists of the following steps:

1. The precipitation of brucite $(Mg(OH)_2)$ and aragonite $(CaCO_3)$ at the catholyte, consuming 100% of initial [Mg] and 20% of initial [Ca] in seawater.

2. Catholyte processing. This consists of residual Ca^{2+} precipitating as $CaCO_3$ while Mg(OH)₂ solids are discharged into the ocean or by other processes resulting in the production of hydrated Mg carbonates.

3. The realkalinization of the analyte stream to neutralize its acidity and replenish divalent cations that are consumed during mineral precipitation.

4. The discharge of the processed analyte and catholyte streams back into the ocean.

The Equatic process's mass balances were examined for a system that removes 1 t of

CO₂ per day (TPD), with 4.6 kg of CO₂ removed per m^3 of seawater processed at the catholyte.

The result is the conversion of seawater CO_2 into mineralized form and alkalization of the ocean.

The authors state in this 2023 paper that the uncontrolled discharge of the anolyte (i.e., an acidic solution) effluent into the ocean **could result in changes in seawater chemistry and saturation states.** To counter such effects would require the **realkalinization of the effluent** by the dissolution of alkaline minerals such as those found in mafic and ultramafic rocks, into the anolyte to elevate the concentrations of divalent cations. This translates to a theoretical mass requirement of 1.60 tons Mg₂SiO₄/ton CO₂ sequestered or 2.36 tons CaAl₂ Si₂O₈/ton CO₂ to replenish Mg²⁺ or Ca²⁺ removed by precipitation of Mg–CO₃ hydrates and CaCO₃. Obviously, this would require the activation the mining of large amounts of ultramafic rocks.

Several of the La Plante et al co-authors are from the UCLA's Institute for Carbon Management. They have founded a company called **Equatic** utilizing this technology.

OAE In conclusion, a range of techniques have been proposed for increasing ocean alkalinity, which exploit numerous reaction pathways. However, two of them, OAE and eOAE require the mining and processing, of olivine. It may also be possible to use faster dissolving minerals such as CaO, MgO, Mg(OH)₂ for alkalinity addition. Some components of these processes already operate at a large scale (e.g., the production of lime). Upscaling these processes to have an impact on anthropogenic CO₂ emissions (i.e., billions of tons CO₂/yr) is a considerable challenge.

Finally, the modification of the ocean raises issues surrounding regulation, monitoring, and the distribution of impact (Rayner et al, 2013). The **London Convention/Protocol** was created to limit dumping of materials in the ocean and has been amended (yet to be ratified) to include marine geoengineering proposals. More work is required to develop governance for ocean alkalinity carbon storage, but this should be informed by, and tailored to, the potential harms and benefits of specific alkalinity addition approaches.

Examples of some OAE Projects (Yeung, 2021)

Riebesell et al (2023) completed one of the first actual OAE research projects. It was carried out on the Canary Islands and placed crushed limestone into the ocean. Dr. Riedesell is a marine biologist at GEOMAR Helmholtz Center for Ocean Research in Kiel, Germany. The

project was supported by EU funds and included a team of 35 researchers. Riebesell stated, "...what's certain is that **alkalinity enhancement has enormous potential**."

The 33-day experiment was caried out in 8,000-liter thermoplastic **polyurethane mesocosms** mixed with varying amounts of crushed limestone. The rock reacts with water, and during that reaction takes up CO_2 from the atmosphere. Alkalinity levels ranging from normal to two-fold enhanced were tested and 45 parameters were examined.



Mesocosms and testing of OAE (Yeng, 2021)

<u>Riebesell estimated that scaled up enhanced weathering could sequester up to 100 gigatons</u> of CO₂ per year.

"Rosalind Rickaby, a professor of biogeochemistry at Oxford University's Department of Earth Sciences has for the past two years conducted lab research into whether calcification occurs, when alkalinity is increased, in cultures of single-celled organisms called coccolithophores and foraminifera. She's seen positive signs." (Yeung, 2021).

In 2022 the team plans a second project in the waters of Norway using 50,00-liter mesocosms. This will include testing how fish are affected. Although limestone was used in this initial test, the most promising option is olivine that, pound for pound, which sequesters twice as much CO₂ as quicklime and four times as much as limestone. Olivine will be used in the Norway research.

Project Vesta. A separate research program undertaken by this San Francisco, California-based company **also plans to deploy olivine in four field trials** across the coastal waters of North Carolina, New York, India, and the northern Caribbean in the next few years. "It's found all over the world, even on Hawaiian beaches," says CEO Tom Green. "Its mining doesn't require any chemicals, you just have to extract it, and you could use the world's coal mining infrastructure."

In a 2023 study by Vesta, 400 m³ of olivine were added to 400 meters of the North Sea Beach coast in California. Early monitoring using closed chambers on the sea floor **they have yet to show any heavy metals building up in invertebrate worms and mollusks.** A potential problem was that the olivine sank below the surface, potentially reducing its effectiveness.

Studies of the extent of alkalinization and efficiency of removal of CO_2 are in progress (Tollefson, (2023). They obtained the olivine from Norway.

Planetary Technologies (2023) a Canadian Company, is using magnesium hydroxide in its OAE study. They released four tons of $Mg(OH)_2$ into wastewater from a sewage treatment plant in Cornwall, UK. It was carried 11 km out to sea in a discharge pipe. Since the manufacture of $Mg(OH)_2$ was energy intensive, they plan to shift to brucite, a natural source of $Mg(OH)_2$. They are evaluating whether the alkalinized sea water remains at the surface to adsorb atmospheric CO₂ or whether it sinks, greatly delaying the effectiveness of CO₂ adsorption (Tollefson, (2023).

Conclusions about OAE using Olivine. The modeling by **Fakhraee et al (2023)** places some sobering limitations on the use of olivine in OAE. By contrast the use of CaO and especially MgO and Mg(OH)₂ does have promise. The use of CaO has the disadvantage that a lot of CO₂ is released during its production, negating its use. MgO or Mg(OH)₂ is thus preferred. Despite the computer-based conclusions of Fakhraee et al (2023), Riebesell's expanded microcosm studies still plan on using olivine.

Direct Removal of CO₂ from the Ocean without Ultramafic Rocks

The advantage of extracting CO_2 from sea water is that the concentration of CO_2 in sea water is 80+ times greater than in the atmosphere. There would be many advantages to an electrolytic process that removes CO_2 from seawater and converts it to carbonates without requiring the addition of olivine or other alkaline rocks or chemicals.

Ho, H-J. and Izuka, A. (2023) This review article assesses the concept and mechanism of mineral carbonation for CO₂ sequestration using seawater. They point out that mineral carbonation can make a substantial contribution to CO₂ emissions reduction and negative emissions required to limit global temperature change to less than 2°C. Seawater is alkaline (pH: 8.0-8.2) with abundant content of Ca++ (0.41 g/l) and Mg (1.29 g/l), which can react with CO₂ via mineral carbonation to form carbonated products.

They state that the addition of an alkaline agent is not necessary because seawater has relatively alkaline properties and higher content of Ca²⁺ and Mg ²⁺, but it is recommended to keep the pH in a certain range (within 8.0–8.2) reported from the literature, and the mineral carbonation reaction can directly proceed to produce carbonated products to achieve CO₂ sequestration and utilization.

The relative proportion of CO_3^{2-} ions, with respect to CO_2 will be appreciably higher in seawater than in freshwater (see Bjerrum Plot page 155). While the authors reviewed three types of seawater (natural seawater, desalination brine, and seawater-based wastewater), **the use of natural seawater is of interest here.** Seawater carbonation can be classified as **direct aqueous carbonation and indirect carbonation**. The reactions for these two processes include the use of electrolysis, are reviewed. Due to the greater CO_2 solubility in seawater, enhancement of carbonate precipitation can improve CO_2 fixation as stable solids.

Direct aqueous carbonation is a single process in one reactor. It is based on three main reaction steps:

(i) Ca/Mg extraction from alkaline materials,

(ii) CO₂ dissolution, and
 (iii) CaCO₃/MgCO₃ precipitation.
 These reaction steps are concurrent and involve three phases (gas, liquid, and solid).

The CO_2 gas is dissolved in seawater according to Henry's law which states that at a constant temperature, the amount of a given gas that dissolves in a liquid is directly proportional to the partial pressure of that gas in equilibrium with that liquid.

C = kP

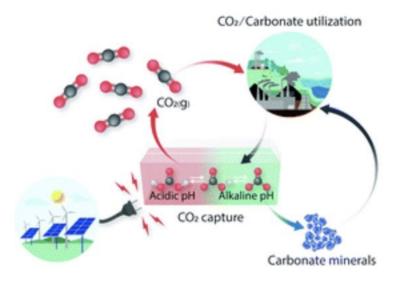
where C = the concentration of the dissolved gas, k = Henry's constant, and P = the partial pressure of the gas.

Even though the addition of an alkalinizing agent is not necessary the CO_2 dissolution ability in seawater is increased with the increase in pH and reaches more than 100 times greater than that without alkaline substance addition, showing that pH is critical to improving the CO_2 dissolution ability in seawater.

For indirect carbonation, there are two main electrochemical methods for mineral carbonation, membrane electrolysis and **BPED** (bipolar membrane electrodialysis). With the later the major problem is membrane fouling occurred by the impurities, decreasing the membrane's life, reaction efficiency, and increasing the process cost. Theoretically, mineral carbonation with BPED does not require additional chemical addition because the BPED system can regenerate acidic and alkaline solutions.

Karoui, et al (2013) reported that in seawater, the application of cathodic electricity, a scale layer forms on the metal surface. The scale was composed mainly of CaCO₃ (aragonite) plus Mg(OH)₂ (brucite).

Sharifian et al (2021) have reviewed the various approaches to the use of electrolysis to capture CO₂. A common theme is the use of electrolytically produced **pH-swing** whereby CO₂ can be captured and recovered by shifting the pH of a working fluid between acidic and basic pH. Such swing can be applied electrochemically through electrolysis, bipolar membrane electrodialysis, reversible redox reactions and capacitive deionization. The swing is only about 2 pH units around neutral. The following is an example of pH-swing.

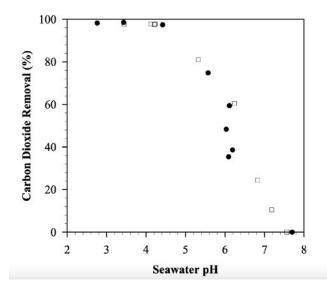


Datta, S.et al (2013) presented an electrochemical method for CO_2 capture from coalfired power plant **flue gas**. The method utilized *in-situ* electrochemical pH control with a resin wafer electrodeionization (RW-EDI) device that continuously shifts pH of the process fluid between basic and acidic in sequential chambers (**pH-swing**). This pH-swing enables capture of CO_2 from flue gas in the basic chamber followed by release (recovery) of the captured CO_2 (**purified**) in the acidic chamber of the same device.

Dimascio, F. F. et al (2010); Willauer, F. et al (2017). This was a study by the Naval Research Laboratory to examine the feasibility of producing jet fuel at sea to support carrier flight operations. **Extracting carbon dioxide from seawater** was part of a larger project to create liquid hydrocarbon fuel at sea. CO_2 as a carbon feedstock could be catalytically reacted with hydrogen to form diesel and/or jet fuel. The hydrogen could be produced through electrolysis of water and the electrical energy for this process would be derived through nuclear power. Based on the Bjerrum Plot (page 155) H₂CO₃ predominates at lower pH. Given the reversibility of the equation,

$$CO_2(aq) + H_2O \rightleftharpoons H_2CO_3(aq)$$

CO₂ is readily degassed at pH below 5.



From Dimascio, F. F. et al (2010)

In summary, an electrochemical **acidification cell** was developed and studied to determine if it could be used as a feasible and practical method for sequestering large quantities of CO_2 from seawater. This indirect path captures bound CO_2 in the form of bicarbonate from seawater. They concluded that electrolysis driven acidification of sea water was an effective method of extracting CO_2 from seawater.

Willauer, F , DiMascio F and Hardy, D R et al (2017a,b) is the same Naval research group as above. Before their process could become feasible, methods had to be developed to extract large quantities of CO₂ and H₂ from seawater fast and efficiently. To this end, commercially available electrodeionization cells were modified by National Renewable Energy Laboratory to function as **Electrolytic Cation Exchange Modules (E-CEM).** They were able to increase the processing rate from 0.5 gallons per minute to 25 gallons per minute.

Yang et al. (2023) reported that an organic catalyst containing amide groups had extremely high activity and selectivity for chlorine production in the chlor-alkali process. The addition of CO₂ to the reaction gave rise to the NCOOH intermediate that exponentially enhanced catalytic efficiency. This helped to reduce the energy demands for chlorine production by 2 -5%. On the negative side, the Yang et al (2023) technique substituted O₂ production for the H₂ production. Loss of electricity from H₂ fuel cells, would remove 50% of the recyclable electricity, which is much more than the 2-5% the organic catalyst would gain.

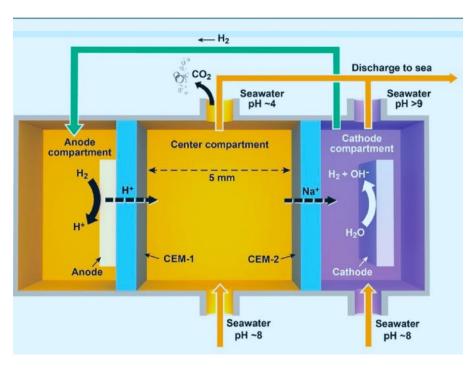
Oloye and O'Mullane, (2021) proposed a CO₂ capture, conversion and utilization technology that can be **powered by renewable energy with the potential to mitigate CO₂ emissions**. This relies on **an electrochemical process whereby the dissolution of carbon dioxide into carbonate ions is accelerated via a locally induced pH change at the cathode**. The chemical reactions involved are similar to those in the La Plante et al (2021) paper. The carbonate ions can then be complexed with metal cations such as Ca^{2+} , Sr^{2+} or Mn^{2+} present in solution to form their respective **metal carbonates, CaCO₃, SrCO3 and MnCO₃, which precipitate out of solution**. To ensure the cathode is not fouled by deposition of the insulating

metal carbonate, the process is **operated under hydrogen evolution conditions** thereby alleviating any significant attachment of the solid to the electrode. They demonstrated this process in CO₂ saturated solutions as well as the possibility of direct air capture whereby the precipitation of CaCO₃ from atmospherically dissolved CO₂ during electrolysis was observed. The latter process could be **significantly enhanced via the use of 5 % v/v of monoethanolamine (MEA)** in the electrochemical cell to increase the solubility of CO₂. Finally, the process was investigated using **seawater** which is also shown to be successful after the initial precipitation of metal sulfates from solution. In particular, the use of renewable energy to capture CO₂ and create CaCO₃ while also generating hydrogen may be of particular interest to the cement industry which has a significant CO₂ footprint.

The method also has the added advantage of **generating clean hydrogen** if operated by renewable energy sources. **This could provide additional renewable energy via fuel cells.**

The mineralization of the CO_2 in the form of $CaCO_3$ has the advantage of avoiding the potential danger of underground storage of gigatons of CO_2 gas and avoiding the need to mine and grind and distribute gigatons of climate rocks.

Yan, L et al (2022) Described an Electrochemical Hydrogen Looping (EHL) system that capitalizes on the generation of a proton (H^+) and OH⁻ from seawater. A CO₂ capture efficiency was as high as 91%. They proposed that the EHL system can remove CO₂ from simulated seawater at a record low electric energy consumption of 660 kWh/t CO₂. This was a significant reduction of 56% compared with the bipolar membrane electrodialysis technology. They concluded that the EHL flow cell with its much lower energy consumption provided an economical approach for direct removal of CO₂ from seawater at practical scale.



The following is their diagram of the method.

Schematic of the EHL cell for removing of CO₂ from seawater (CEM-1, proton exchange membrane; CEM-2, sodium ion exchange membrane; cathode, Pt/C

catalyst coated carbon electrode (CP-ESA, SGL Carbon); anode, Pt/C catalyst coated carbon paper (Sigracet 22 BB, SGL Carbon); the volume of hydrogen in the anode compartment is 50 mL at 1 atm; no seawater flows through the anode chamber).

At the anode, the oxidation of hydrogen will release two protons per hydrogen molecule.

$$H_2 - 2e^- \rightarrow 2H^+$$

At the center compartment, these protons react with CO_3^{2-} and $HCO_3 -$ to release CO_2 gas for collection.

 $H^+ + HCO_3^- \rightarrow H_2O + CO_2 (g)$

and produce acidified seawater with a pH from 4 - 5.6. $2H^+ + 2NaCl \rightarrow HCl + 2Na^+$

At the cathode NaOH is formed producing a basic solution which is released to the ocean to combat ocean acidification.

$$H_2O + 2Na^+ + 2e^- \rightarrow H_2(g) + 2NaOH$$

The H₂ is returned to the anode, thus the term, electrochemical hydrogen-looping (EHL). With EHL the electrical cost of 660 kWh per ton of CO_2 is considerably lower than the La Plante (2021) figure of 2,270 kW/t CO_2 .

In their supplementary material, the authors compare the efficacy of EHL to other techniques where BPMED-1 and BPMED-2 refers to bipolar membrane dialysis, E-CEM to electrolytic cation exchange modules, and DAC to direct air capture.

Technology	Theoretical voltage (V)	Electricity energy consumption (kwh/ton CO ₂)	Current density (mA/cm ²)	Catalyst usage	Operation conditions and other remarks
EHL	0.48	~660	50	Pt catalyst	Need an amount of hydrogen; low cost and low energy consumption
BPMED-1	0.83	~1400	<10	Pt catalyst	Need extra Na ₂ SO ₄ / H ₂ SO ₄ , low operation current density and high energy consumption
BPMED-2	0.36	~920	<10	No catalyst	Need extra K ₃ Fe(CN) ₄ /K ₄ Fe(CN) ₄ , low operation current density due to slow kinetics of water splitting on bipolar membrane
E-CEM	1.71	~20000	20-61	Previous metal catalyst	High energy consumption but produce hydrogen fuel
DAC-H ₂ - recycling	Not reported	~2300	2.5-15	Pt catalyst	Low energy consumption
DAC-pH swing	Not reported	~300	50	No catalyst	Low energy consumption and high operation current density

Other than DAC-pH swing (see below), EHL had the lowest electrical energy requirement of the other six (including that of La Plante et al (2021). While EHL may help to solve the problem of the high energy cost of DACS, like DACS **the CO₂ still must be buried**.

Kim, S. et al (2023) described a two-electrode silver-bismuth systems operating in tandem in a cyclic process, one acidifying the ocean water, and the other regenerating the electrodes through alkalization of the treated stream. CO_2 can be continuously removed from simulated oceanwater with a relatively low energy consumption of 122 kJ/mol, and high electron efficiency. The goal of the authors was to avoid the need for introducing chemicals to the anode and cathode half cells and to avoid the use of membranes, thus decreasing costs.

The process is cyclic: It first acidifies the water to convert dissolved inorganic bicarbonates to molecular carbon dioxide, which is collected as a gas under vacuum. Then, the water is fed to a second set of cells with a reversed voltage, to recover the protons and turn the acidic water back to alkaline before releasing it back to the sea. Periodically, the roles of the two cells are reversed once one set of electrodes is depleted of protons (during acidification) and the other has been regenerated during alkalization.

As with the Yan et al (2022) approach, the disadvantage of this is that the released CO₂ must be buried.

Jin, S et al (2022) describe a DAC-pH swing, low energy carbon capture technique for extraction of CO_2 from sea water. Although it has the advantage of using less electrical energy, 300 kW/ton of CO_2 (see last line of above table) like several others described above, it has the disadvantage that the captured CO_2 must be buried. In addition, it utilizes a complex proton transfer complex sodium (3,3'-(phenazine-2,3-diylbis(oxy))bis(propane-1-sulfonate)) (DSPZ). It is uncertain whether this requirement would limit expansion to gigaton levels.

Carbonic anhydrase. The techniques of Yan et al, (2022), Kim et al (2023) and Jin et al 2022) require less electricity than the La Plante et al (2021) technique but they all had the disadvantage that they produce CO_2 which must be disposed of. This raises the question, "Is there an inexpensive way to convert CO_2 gas to carbonates?" One possibility is the use of carbonic anhydrase, CA, which catalyzes the reaction,

Alvizo et al, (2014) used mutation driven evolution to develop a carbonic anhydrase variant, DvCA, that provided a 4-million-fold improvement over the natural enzyme and was tolerant of extreme conditions. They proposed to use DvCA to recover CO_2 from flue gas. Various companies can produce this enzyme in large quantities. One potential way of using DvCA is in a bioreactor with carbonic anhydrase co-valiantly linked to the reactor (Blais and Rogers, 2003). The HCO₃⁻ could be put back into the ocean to react with Ca++ to form CaCO₃ and the hydrogen could be used in fuel cells to supplement the electricity requirements. Issues of the stability of CA needs to be addressed. For example, Is DvCA more stable than the natural CA? Does co-valiantly linking CA to a bioreactor make it more stable?

NAS (2022b) Chapter 8 Electrochemical Engineering Approaches of a document entitled A Research Strategy for Ocean-based Carbon Dioxide Removal and Sequestration. Washington, DC: The National Academies Press. provides a thorough 29-page review of electrochemical methods for the direct removal of CO₂ from the ocean.

It is possible to use electrochemical processes to increase the alkalinity of seawater, and/or to force the precipitation of solid alkaline materials. In the former process, reactions at the cathode increase the alkalinity of the surrounding solution, which can then be discharged into the ocean. In the latter, the reaction cell is separated by an ion-selective membrane, a physical barrier, or internal hydrodynamics, and seawater or brine is introduced into the cathode compartment (Rau et al., 2013; Zhao et al., 2020; La Plante et al., 2021; Oloye et al., 2021). The potential difference across the cell promotes the migration of ions (usually sodium) across the barrier/cell, and ultimately promotes the formation of solid metal hydroxide residues (e.g., brucite or portlandite) that could be added to the ocean to increase its alkalinity.

Acid and Basic approaches have been proposed to extract CO_2 from seawater. Basic approaches exploit high-pH conditions created around the cathode to shift the equilibrium of the carbonate system toward a greater concentration of bicarbonate and/or carbonate ions (La Plante et al., 2021). This creates conditions in which carbonate precipitation can occur and promotes an increase in aqueous CO_2 . Dissolved inorganic carbon is removed and collected as solid carbonate residues. They state (p209) that "Basic approaches exploit high-pH conditions created around the cathode to shift the equilibrium of the carbonate system toward a greater concentration of bicarbonate and/or carbonate ions (La Plante et al., 2021). This creates conditions in which carbonate precipitation can occur and promotes an increase in aqueous CO_2 , which may be evolved and collected similarly to the acid approach (Rau, 2008; de Lannoy et al., 2012). Dissolved inorganic carbon is removed and collected as both solid carbonate residues and as evolved CO_2 gas. Basic approaches that force the precipitation of solid carbonate without restoring alkalinity do not result in the net removal of CO_2 from the atmosphere, although they reduce the concentration of CO_2 that is dissolved in solution."

These two broad categories of ocean CDR electrochemical engineering are, in some cases, not mutually exclusive, and could be deployed as a <u>hybrid approach that both extracts</u> <u>CO₂ from seawater</u>, in the form of a gas, <u>or as mineral carbonates</u>, while increasing the <u>alkalinity of the effluent solutions thus resulting in the net removal of CO₂ from the atmosphere.</u>

The following table summarizes the different approaches to CDR.

TABLE Summary of Ocean-Based Electrochemical Approaches for CDR from the Atmosphere

Direct CDR—acid process. The acid stream from the anode in the electrochemical cell is used to decrease the pH of seawater to evolve CO₂. The base stream from the cathode is then mixed with the decarbonized seawater to capture additional CO₂ from the air, resulting in a continuous closed cycle where CO₂ is effectively removed from the air via seawater.

Direct CDR—base process the base stream from the cathode in the electrochemical cell is used to precipitate carbonate from seawater with or without the evolution of CO₂.

Ocean alkalinity enhancement (OAE)— Using seawater as the electrolyte, sodium hydroxide (NaOH) is concentrated at the cathode (which is added to the ocean to increase alkalinity. The acid stream from the anode is neutralized through reaction with silicate rocks.

OAE—water electrolysis Similar to seawater/brine electrolysis but using an alternative non-NaCl-based electrolyte (e.g., based on Ca or Mg).

OAE—salt recirculation Similar to seawater/brine electrolysis but the salt form, through reaction with silicates, is recycled back into the catholyte.

Hybrid approaches A combination of electrochemical approaches that results in an increase in ocean alkalinity and the removal of CO₂ from seawater, e.g., as a gas, or in mineral carbonates.

Monitoring and Verification Electrochemical methods, on account of being contained engineering processes, are readily amenable to assessments of mass, energy, and CO₂ balances, that is, both embodied in and as related to CDR.

Energy Requirements House et al. (2007) consider electrolysis of seawater and suggest energy requirements **between 0.8 and 2.5 MWh/t CO2 removed**, which is consistent with Rau (2008), Rau et al. (2013), Davies et al. (2018), and La Plante et al. (2021), who calculate 1.5–2.3 MWh/t CO2 for similar systems.

Eisaman et al (2011, 2012, 2020): Electrochemical Extraction of CO₂ from Seawater Eisaman and colleagues (Eisaman et al, 2011, 2012; de Lannoy et al, 2018; Eisaman, 2020) described an electrochemical process of extracting CO₂ from seawater using a bipolar membrane electrodialysis system (BPMED). They demonstrated the ability to extract 59% of the total dissolved inorganic carbon from seawater as CO₂ gas with an electrochemical energy consumption of 242 kJ molÀ1 (CO₂). **This was then converted into fuel.** Eisaman and his team of researchers founded **SEAMATE (Safe Elevation of Alkalinity for the Mitigation of Acidification Through Electrochemistry**).

One configuration, termed the 'base process', added base to the seawater to shift the carbonate buffer system towards carbonate ions, which precipitated as $CaCO_3$. A closed loop cycle was achieved by returning this decarbonized and alkalinized brine to the ocean for additional CO_2 absorption from the air. With continued research they hoped to simplify the process and decrease costs.

In a U.S. Patent (Eisaman 2023) reported using the BPMED method to produce NaOH and HCl from the electrolysis of sea water. The NaOH was used for OAE while the HCl was kept on shore for commercial sale. This approach would not be suited for placement on ships.

Ebb Carbon is a start-up using an electrolysis system that can fit into a 20-foot shipping container. The company is led by Matt Eisaman (above) and Ben Tarbell. Its current location is a waterfront laboratory in Sequim Bay, on Washington's Olympic Peninsula and is run in cooperation with the Department of Energy's Pacific Northwest National Laboratory (PNNL). Seawater is run through a series of ion selective membranes and produces an acidic stream of HCl and a basic stream of sodium hydroxide. The sodium hydroxide stream is used to alkalinize the effluent seawater while **the acidic HCl stream is kept on land**. At a gigaton level there are two potential problems. First, what to do with the gigatons of strong HCl acid stored on land? Second, since it is land bound it cannot be placed on ships to provide OAE throughout the ocean. HeOAE (see below) avoids these problems.

Xie et al (2015) proposed a novel method, based on membrane electrolysis, for carbonation and separation of calcium and, magnesium ions from sea water using low voltage. Compared with traditional electrolysis, membrane electrolysis can reduce the required voltage by about 1.3 V, which reduces the energy consumption for CO₂ mineralization dramatically. This could potentially work as the first half of the HeOAE technology since it would significantly reduce the amount of renewable electricity required.

According to this study, 1000 m^3 of concentrated seawater could mineralize 4.65 tons of CO₂. In addition, 9.97 tons of magnesium carbonate hydroxide and 2.02 tons of precipitated calcium carbonate could be produced with only a total electric power consumption of 5,676 kWh. Based on these figures the Hie et al (2015) technique required approximately half the electricity per ton of CO₂ sequestered as the LaPlante technique.

This technique also has the potential of providing both halves of the hybrid heOAE, with the second half providing for alkalinization of the effluent by the production of Mg carbonate hydroxide.

The Xie et al (2015) emphasis was the use of this technology to remove salts from hard water and in the process produce commercial amounts of chemicals. However, for our purposes it seems like it could also be placed on catamarans and used to both mineralize CO_2 and alkalinize the seawater combining the two hybrid halves into one. Further research is needed to validate this potential.

Digdaya, et al (2020) Extraction of CO₂ from Seawater for Fuel. These authors also describe a bipolar membrane electrodialysis system (BPMED) of extracting CO₂ from seawater similar to Eisaman, et al. The CO₂ is also converted to fuels and chemicals such as carbon monoxide, ethylene, ethanol, and propanol with total Faradaic efficiency (FE) of up to 73%.

Rabinowitz, J. A. and Kanan, M.W. (2020) Preferential Formation of CO_3^{++}. These authors point out that when electrolysis is used to generate multicarbon products such as methane, ethylene, ethanol, and propanol, the biggest obstacle to improving performance is an often-overlooked basic chemistry problem: the rapid and thermodynamically favorable reaction of CO_2 with hydroxide (OH–) to form carbonate (CO_3^{2-}).

Gagern et al, (2022) reviewed seven different methods of ocean-based CDR of which OAE was one. This was a review for Marine Technology Society. They state one of the most promising approaches is ocean alkalinity enhancement.

Electrochemical weathering of alkaline minerals has received attention from startups such as **Planetary Hydrogen**, **Sea Change**, and others) because of marketable side products. In contrast to adding alkalinity, **electrodialysis can remove acid from seawater in the form of CO₂ or hydrochloric acid (HCl)**, thus allowing the remaining alkalinity to draw in atmospheric CO₂ upon return to the ocean. To effect safe CDR, the CO₂ and/or HCl must be sequestered or consumed. **Ebb Carbon** is leading this effort in the United States.

Tyka et al (2022) Pumping Acidified Surface Water to Deep Ocean Tyka et al (2022) presented a **method of alkalinization which relies purely on the redistribution of acidity from a thin layer of the surface ocean to a thicker layer of deep ocean**. They state that little attention has been paid to the alkaline carbonate sediments (CaCO₃) in the deep ocean and accelerating the dissolution of these sedimentary carbonate minerals has not yet been explored.

Their approach of pumping surface acidity into deeper ocean layers could provide a means to induce the dissolution of the alkaline mineral deposits in the deep ocean while accelerating CO_2 uptake at the surface. The inventory of erodible $CaCO_3$ on the ocean floor is estimated to be about 1,600 GtC, theoretically more than sufficient to compensate for the 640 GtC that humanity has released since preindustrial times.

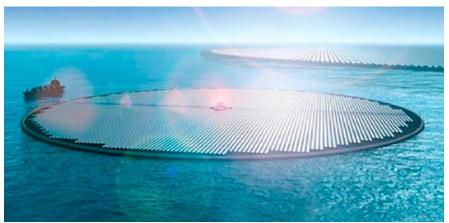
As with heOAE, expensive mining, grinding and distribution of alkaline material is eliminated. No terrestrial material is added to the ocean, avoiding significant alteration of seawater ion concentrations or issues with heavy metal toxicity. Based on their simulations they estimated 1–3 GtC or 3.7 to **11 GtCO₂ per year** could be removed over a 50-year period. The permanence of the CO₂ storage depends on the depth of acid pumping. At 43,000 m, approximately 85% is retained for at least 300 years, and <50% for at least 2000 years.

They suggest the cost per ton of CO₂ would be competitive with terrestrial direct air capture and other negative emissions technologies while avoiding the ecological impacts of accelerated mineral weathering.

Patterson et al (2019) Methanol Islands. These authors proposed the use of solar energy to recycle atmospheric CO₂ into methanol by the following equation:

$$3H_2 \ + \ CO_2 \rightarrow CH_3OH + H_2O$$

They envisioned clusters of marine based floating islands, on which photovoltaic cells convert sunlight into electrical energy to produce H_2 and to extract CO_2 from seawater, where it is in equilibrium with the atmosphere. These gases are then reacted to form methanol which is shipped to the end consumer.



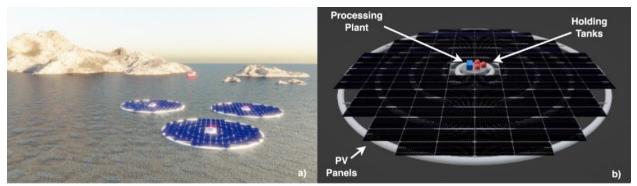
Artist's conception of solar islands in the open ocean

The problem with this idea is that in sum it does not contribute to the reduction of CO_2 in the atmosphere since methanol burns by the following equation:

$$2CH_3 \ OH \ + \ 3O_2 \ \rightarrow \ 2CO_2 + 4H_2O$$

Keller, D. Jr. et al (2022) also proposed methanol islands, powered by solar or wind energy. They capture CO_2 from the ocean and combine it with hydrogen gas to produce a synthetic fuel. The island components include a carbon dioxide extractor, a desalinator, an electrolyzer, and

a carbon dioxide-hydrogen reactor to complete this process. As with the Patterson proposal, it does not decrease atmospheric CO₂ because burning methanol returns CO₂ to the atmosphere.



Artistic rendering of solar methanol island. (a) shows the device in a potential deployment scheme, serviced by a tanker ship. (b) shows a close-up of the device with its different main components: the floating structure and solar panels, the processing plant, and the holding tanks for the produced methanol. (Keller, et al, 2022)

Hartmann, J. et al (2023) was concerned about the stability of alkalinity when added to seawater. They point out that the ocean surface is already supersaturated with respect to two forma of Ca carbonate, calcite and aragonite, and that an increase in total alkalinity (TA) together with a corresponding shift in carbonate chemistry towards higher carbonate ion concentrations would result in a further increase in supersaturation, and potentially to solid carbonate precipitation. Precipitation of carbonate minerals would consume alkalinity and increase dissolved CO_2 in seawater, thereby reducing the efficiency of OAE for CO_2 removal.

To examine this, they performed a set of six experiments using natural seawater with alkalinity of around 2400 μ mol kgsw⁻¹. The application of CO₂-equilibrated alkaline solution bore the lowest risk of losing alkalinity due to carbonate phase formation if added total alkalinity (Δ TA) was less than 2400 μ mol kgsw⁻¹. By contrast, the addition of reactive alkaline solids can cause a net loss of alkalinity if added Δ TA > 600 μ mol kgsw⁻¹ (e.g., for Mg(OH)₂).

Commercially available (ultrafine) $Ca(OH)_2$ causes, in general, a net loss in TA for the tested amounts of TA addition, which has consequences for suggested use of slurries with alkaline solids supplied from ships. The rapid application of excessive amounts of $Ca(OH)_2$, exceeding a threshold for alkalinity loss, resulted in a massive increase in TA (> 20 000 µmol kgsw⁻¹) at the cost of lower efficiency and resultant high pH values > 9.5. Analysis of precipitates indicated the formation of aragonite. However, unstable carbonate phases formed can partially redissolve, indicating that net loss of a fraction of alkalinity may not be permanent, which has important implications for real-world OAE application.

Their results indicated that using an alkaline solution instead of reactive alkaline particles can avoid carbonate formation unless alkalinity addition via solutions shifts the system beyond critical supersaturation levels. To avoid the loss of alkalinity and dissolved inorganic carbon (DIC) from seawater, the application of reactor techniques can be considered. These techniques produce an equilibrated solution from alkaline solids and CO₂ prior to application. Differing behaviors of tested materials suggest that standardized engineered materials for OAE need to be developed to achieve safe and sustainable OAE with solids.

These results favor the heOAE technology (see below), since its output is in the form of an alkaline solution, i.e., alkaline seawater.

In conclusion, the extraction of CO_2 from seawater has the advantage that water holds 80+ times the concentration of CO_2 as the atmosphere. Several methods extract CO_2 from seawater and convert it into carbonates which are returned to the oceans. Unlike DACS there is no need to bury gigatons of CO_2 . Several alternative techniques with lower power requirements remove CO_2 from seawater and produce CO_2 gas. Some propose to convert that CO_2 into fuel but when that is burned it releases CO_2 back into the atmosphere.

HeOAE. It is likely that the use of two parallel electrolysis techniques as in the hybrid approach would be the most useful thus the name heOAE for hybrid electrolysis OAE. One of the two arms of the hybrid could be that of La Plante et al (2021, 2023) or others (see above), to produce the carbonates. The second arm would be the production of OH⁻ and NaOH at the cathode to alkalinize the seawater. HnOAE would require the electrolysis of water, produced by desalination, rather than seawater. The two half equations, and the full equation for this electrolysis of water are:

Oxidation (anode) $2H_2O(1) \rightarrow O_2(g) + 4H^+(aq) + 4e^-$ Reduction (cathode) $4H_2O + 4e^- \rightarrow 2H_2(g) + 4OH^-(aq)$ Total $2H_2O(1) \rightarrow 2H_2(g) + O_2(g)$

The OH⁻ from the cathode, can be mixed with the brine from desalination, to produce NaOH to alkalinize the seawater. It is important to start with water instead of sea water because the electrolysis of sea water, i.e. the Chlor-alkali Reaction, produces:

 $2 \operatorname{NaCl}(aq) + 2 \operatorname{H}_2O(1) \rightarrow 2 \operatorname{NaOH}(aq) + \operatorname{Cl}_2(g) + \operatorname{H}_2(g)$

Thus, while it produces the desired NaOH to alkalinize the ocean, it also produces an acid, HCl, from the Cl₂ and H₂, which would acidify the ocean. The problem of the production of HCl was solved by Eisaman (2023) by leaving HCl on land and selling it commercially. This would not be amenable to placement on ships such as catamarans. For catamaran based HeOAE the seawater is first desalinated. Then the brine can be added back **after electrolysis** to supply Na⁺ for the OH⁻. This avoids the Chlor-alkali reaction and the production of HCl which would defeat the alkalization of the effluent.

The above shows how, with the electrolysis of water, the **reaction at the cathode** can generate alkalinization of the effluent though the production of OH^- . What about the reaction at the anode? The anode produces $O^2 + 4H^+$. The $2H^+ + 2e -> H_2$ reaction is highly exothermic. H_2 is more stable than $2H^+$. It might be possible to use this heat to drive a small steam turbine to produce electricity. This H_2 plus the H_2 from the cathode can be used in hydrogen fuel cells to produce electricity.

The following summarizes the HeOAE NET:

E#1 Seawater + $CO_2 \rightarrow CaCO_3$ carbonates \rightarrow sequestration of CO_2

Deionizer \rightarrow brine + water

+

E#2 water \rightarrow OH- + brine \rightarrow NaOH, MgOH \rightarrow alkalinization of ocean

A Ship Based Approach for HeOAE.

A ship-based approach, such as a large catamaran, would be ideal for HeOAE. The following are some of the many advantages to this.

• The sails on a catamaran would allow the boat to go anywhere in the ocean at a zero-carbon cost.

• Both halves of the hybrid technique produce H_2 Using fuel cells, a ton of H_2 can produce 16.68 MWh electricity. While this is not enough to provide all the electricity needed, it can definitely help.

• Ships would avoid the NIMBY and most governance issues.

• The ships would each have a laboratory for monitoring pH, pCO₂, carbonates and bicarbonates and other variables of the surrounding ocean. Since it would be unrealistic to perform all of these analyses on board (Dickson, A. G. et al (2007), the emphasis will be on collecting and storing samples for analysis at a centralized experienced land based laboratory.

• Some of the needed electricity could be supplied by onboard solar panels. An example is the following is a SunReef catamaran running on solar energy and sail.



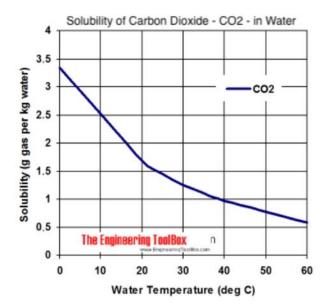
SunReef Solar and Sail Catamaran

However, the electricity produced by such onboard solar panels would not be sufficient to provide the rest of the need electricity. Most of the electricity would be supplied by shore-based solar and wind renewable electricity. Once a proof-of-principle HeOAE catamaran is built this would provide information such as how much CO_2 one ship could sequester as carbonates, after subtracting that supplied by H+ fuel cells how much renewable electricity would be required and other variables.

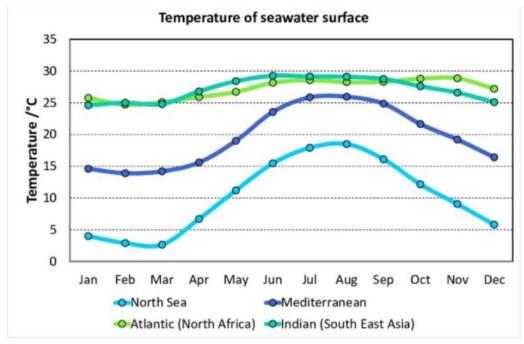
• Batteries would be an important part of the mix. While lithium batteries might work, they probably would not be ideal for ocean travel especially in hot climates. A far better option would be NASA's nickel-hydrogen batteries. They are used in satellites, can last decades, and are temperature tolerant. Currently a disadvantage is the requirement for platinum and palladium. A company is developing Ni-H batteries that may not require these expensive metals. Two additional options are iron-nickel and lithium-sulfur batteries. The electricity from the fuel cells would be stored in these batteries.

• heOAE would avoid any concern about whether the massive deposit of ultramafic rock products in the ocean might pose problems with heavy metal contamination, since heOAE simply uses electricity to rearrange the pre-existing chemistry of the ocean.

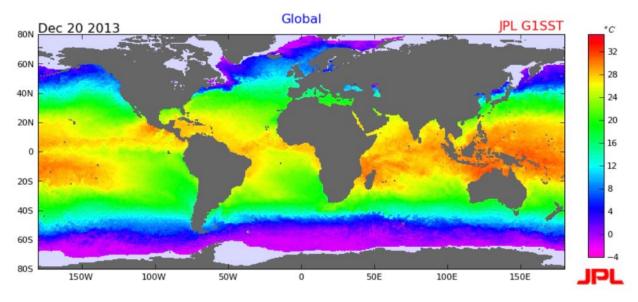
• Being ship based heOAE could concentrate on specific areas of the ocean such as those involved in outgassing of large amounts of CO_2 (pages 165-171) and areas where corals are dying, and areas of the ocean where variations in seawater temperature result in different concentrations of CO_2 . The higher the CO_2 concentration the more effective the HeOAE would be. This is shown in the following figures.



Solubility of CO₂ in water by temperature



Seawater temperatures by season and by region



Seawater temperatures worldwide.

• Although operation in colder water would be desirable much of the operation would have to take place in warmer water.

• The potential use of OTEC (Ocean Thermal Energy Conversion as a source of electricity is examined in the *Addendum*.

• **COPs** Just as the Conferences of Parties obtained the cooperation of most countries to decrease emissions, all countries with access to the ocean could agree to develop one or more recharging sites consisting of solar panels and/or wind turbines next to the ocean. The potential of this is shown below.



Areas of the world suitable for HeOAE charging stations.

Assuming the catamarans could sail hundreds of miles into the ocean, this mix of worldwide charging sites could cover most of the ocean.

In addition to purchasing one or more HeOAE catmamarans, each country would also be responsible for supplying people to crew the boat.

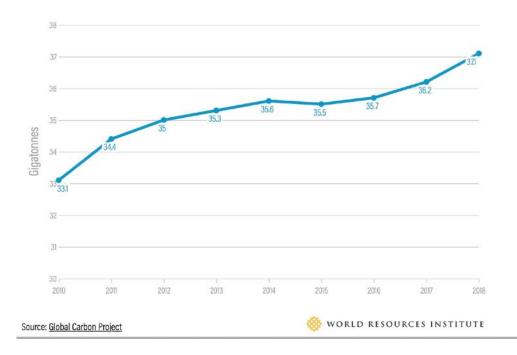
• The huge advantage of ship based heOAE running on renewable energy is that once the boats and onshore solar and wind turbines have been paid for there would be only minimal on-going costs. <u>No need for expensive fuel. No need for gigatons of ground olivine. No need to capture and bury megatons of CO₂. <u>No need to store gigatons of HCL</u>. <u>No huge yearly expenses.</u> This is in marked contrast to the large ongoing costs involved with DACS and climate rock-based EW/OAE. A fleet of HeOAE ships would save many billions of dollars in CO₂ sequestration costs compared to other methods. It is possible that this novel NET could largely combat ocean acidification after 10 years of operation.</u>

END OF SECTION ON Direct Removal of CO2 from the Ocean without Ultramafic Rocks

How much of the Problem of Removing CO₂ from the Atmosphere can be solved by Enhanced Weathering?

A. What are the Annual CO₂ Emissions due to Fossil Fuels?

A common complaint about Enhanced Weathering and indeed any NET is that it accounts for only a small fraction of the total CO_2 emitted per year. Thus, to understand the magnitude of the problem it is **first necessary to determine the amount of CO₂ emitted per year, world-wide.** The following shows the yearly, global rates for fossil fuels from 2010 to 2018.

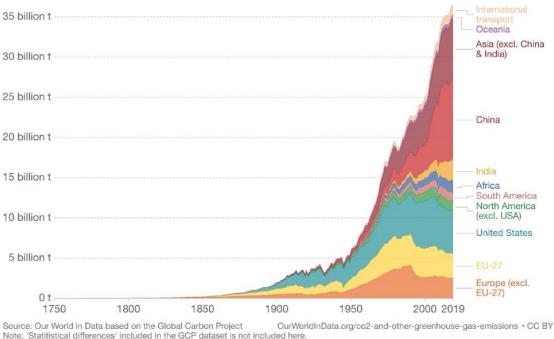


The rate of emissions appeared to be leveling off from 2014 to 2016, but then increased significantly from 2016 to 2018. The levels in 2019 were **36.8 gigatons**.

In his book *How to Avoid Climate Disaster* Bill Gates quotes a figure of **51** gigatons/year. This includes all greenhouse gases and land use emissions of CO₂. Most discussions of NET state that removing 10 gigatons/year by mid-century, is a reasonable goal.

The following figure shows the contribution of each major country.

Annual total CO₂ emissions, by world region This measures CO_2 emissions from fossil fuels and cement production only – land use change is not included.



Our Worl in Data

Based on these figures a rate of emissions from fossil fuels of approximately 37 billion tons/year provides a reasonable estimate.

B. Estimates of the Amount of CO₂ that could be removed by EW.

a. Beerling et al. The Beerling et al (2020) paper has been widely quoted in this review. In this paper Beerling estimated that annually EW could remove 0.5 to 2 Gt CO₂/yr. This was similar to other NET technologies such as direct air capture and storage, biochar, soil organic carbon sequestration, and afforestation/reforestation.

Beerling et al (2018) and Kantola, et al (2017) On the basis of basalt applications of 10 to 50 t ha -/yr to 70×10^6 ha of the annual crop's corn/soy in the corn belt of North America could sequester 0.2–1.1 PgCO₂, **0.2 or 1.1 gigatons** up to 13% of **the global annual agricultural emissions**, in the long run.

Beerling, D. J. et al. (2016) Provisional estimates suggest that amending two-thirds of the most productive cropland soils (9×10^8 ha) with basalt dust at application rates of 10–30 t/ha/yr could perhaps extract 0.5–4 PgCO₂/yr, or **0.5 to 4 gigatons/yr** by 2100 depending on climate, soil, and crop type.

b. Renforth (2012) A maximum carbon capture potential of ~ 0.3 tCO₂/t is suggested for basalt, assuming a sufficiently fine particle size for effective dissolution on decadal timescales.

c. Strefler et al (2018) showed that enhanced weathering is an option for carbon dioxide removal that could be competitive already at \$60 US/t CO₂ removed for dunite, but only at \$200 US/t CO₂ removed for basalt. The potential carbon removal on cropland areas worldwide could be as large as <u>95 Gt CO₂/year for dunite</u> and 4.9 Gt CO₂/year for basalt. The best suited locations are warm and humid areas, particularly in India, Brazil, South-East Asia, and China, where almost 75% of the global potential can be realized.

d. Hartmann & Kempe (2008) report a theoretical global maximum potential of 65 x 10^6 t sequestered C/year if applied homogenously on all agricultural and forested areas of the world. This is equal to 3.67 x 65 or 238 x 10^6 tons of CO₂. These estimates are significantly lower than those of Strefler et al (2018)

e. Moosdorf et al (2014) They stated that very large amounts of rock would be needed to control or reduce the atmospheric CO₂ concentrations substantially with enhanced weathering.

f. Cobo et al (2022) As shown below, these authors reviewed 36 NETs. In their Table 2. they provided estimates of the maximum number of gigatons of CO_2 removed per year for 28 different types of NET. At a max Greenhouse Gas Removal, GGR (Gt/a CO_2 -eq) of 95 Gt/year, EW with olivine was the highest of all NETs listed by a wide margin.

Negative Thinking About EW Negative Emissions Technology

To ensure that we are not guilty of having our heads in the clouds about EW it is important to maintain transparency about the difficulty of the task. The following are some of the many published comments about the difficulties of EW.

EFI Energy Futures Initiative Clearing the Air. A Federal RD& D Initiative and Management Plan for Carbon Dioxide Removal Technologies. Ernest J. Moniz, Chair (2019) Former Head DOE.

To be effective, technological CDR ultimately needs to be deployed at very large scale. The 2018 National Academies of Sciences, Engineering, and Medicine report entitled Negative Emissions Technologies and Reliable Sequestration: A Research Agenda identified the need for CDR at a scale of approximately 10 billion metric tons (GtCO₂) per year globally by midcentury and 20 GtCO₂ per year globally by 2100 to achieve climate goals while accounting for economic growth. Capturing carbon from the environment at that scale would require the creation of new industries comparable in size to the steel, concrete, and petroleum industries of today.

Ciais, et al. (2013) in Fifth Assessment Report of the Intergovernmental Panel on Climate Change

It is likely that Carbon Dioxide Removal (CDR) would have to be deployed at largescale for at least one century to be able to significantly reduce atmospheric CO₂. In addition, it is virtually certain that the removal of CO₂ by CDR will be partially offset by outgassing of CO₂ from the ocean and land ecosystems.

Editorial in Nature (2018) Volume 554:404, February

Negative Thinking – How work on rocks draw carbon from the air shows the scale of the emissions challenge.

"...the effort required is astounding."

"Grinding up 10–50 tons of basalt rock and applying it to each of some 70 million hectares — an area about the size of Texas — of US agricultural land every year would soak up only 13% of the annual global emissions from agriculture. That still leaves an awful lot of carbon up there, even after all the quarrying, grinding, transporting, and spreading."

"It's not hard to see why many climate scientists have dismissed the near-impossible scale of required negative emissions as "magical thinking". Or why the European Academies' Science Advisory Council said in a report this month: "Negative emission technologies may have a useful role to play but, on the basis of current information, not at the levels required to compensate for inadequate mitigation measures."

"The IPCC is now working on a report on strategies to keep warming to under 1.5 °C, which is due to be published later this year. By necessity, those strategies will lean heavily on negative emissions. Scientists must continue to spell out to policymakers the harsh reality of what this would involve, and in the strongest possible terms."

Schuiling and Krijgsman (2006) By the authors calculations, to neutralize the CO₂ currently in the atmosphere, we need to spread a layer of olivine over the whole surface of the earth at about 0.12 cm thickness. If we limit the olivine spreading to the land mass, the thickness of the layer would become 0.4 cm. This is huge!

Hartmann and Kempe (2008) What is the maximum potential for CO₂ sequestration by "stimulated" weathering on the global scale?

Of all the negative thinking articles, this somewhat obscure one in Naturwissenshaften, is the most negative of them all. It is paraphrased as follows.

Natural chemical weathering of silicate rocks is a significant sink for soil and atmospheric CO₂. Previous work suggested that natural chemical weathering may be stimulated by applying finely ground silicate rocks to agricultural areas or forests [enhanced weathering (EW)]. However, it remains unknown if this technique is practical to sequester globally significant amounts of CO₂ under realistic conditions. Applying first estimates of "normal treatment" amounts from a literature review, we report here a theoretical global maximum potential of 65 x 10^6 tons of sequestered C/year, if EW would be applied homogenously on all agricultural and forested areas of the world. This is equivalent to 0.9% of anthropogenic CO₂ emissions (reference period 2000–2005). First, however, the assumed application of EW on most of the considered areas is not economically feasible because of logistic issues, and second the net-CO₂ sequestration is expected to amount to only a fraction of consumed CO_2 due to the energy demand of the application itself (currently $\sim 11\%$). Unless progress in application procedures is provided, the recent realistic maximum net-CO₂-consumption potential is expected to be much smaller than 0.1% of anthropogenic emissions, and the EW would thus not be one of the key techniques to reduce atmospheric CO₂ concentration.

Kohler et al (2010) also illustrated the magnitude of the problem. They calculated that at least 3 Gt of olivine per year must be distributed over tropical soils annually for Enhanced Weathering to consume 1 Gt C/yr. To put this into context at a local scale, global dissolution of 3 Gt of Mg-olivine per year would mean the distribution and dissolution of up to 600 g/m²/yr of olivine **throughout the whole catchment area of the Amazon.** In addition, these estimates do not address the difficulties in distributing olivine powder in remote land areas covered with dense tropical rain forests and neglect a crucial limitation of the chemistry of olivine dissolution, due to the saturation of waters with silicic acid (H₄SiO₄), which would restrict further dissolution of olivine.

Kohler et al (2013) pointed out that it would require 300 large tankers of olivine put in the ocean each year to normalize ocean acidity. Would this be decreased using heOAE?

Anderson and Peters, (2016) The trouble with negative emissions. Reliance on negative-emission concepts locks in humankind's carbon addiction. Science 354:182-183.

"Negative-emission technologies are not an insurance policy, but rather an unjust and high-stakes gamble. There is a real risk they will be unable to deliver on the scale of their promise."

They raise a common concern about NET, that they would lower the pressure to decrease emissions. However, <u>all NET proposals include the conclusion that a stark reduction of</u> <u>emission is still critical.</u>

Nemet et al, (2018) Negative emissions—Part 3: Innovation and upscaling.

The climate change literature consistently cites long time periods involved in scaling up and deploying NET technologies. **We need to significantly accelerate this process.** This urgency is not reflected neither in the Paris Agreements or in most of the literature they reviewed. If NETs are to be deployed at the levels required to meet 1.5°C and 2°C targets, then important post-R&D issues will need to be addressed in the literature, including incentives for early deployment, niche markets, scale-up, demand, and—particularly if deployment is to be hastened—public acceptance.

Taylor et al, (2015) Enhanced weathering strategies for stabilizing climate and averting ocean acidification. Nature Climate Change 6: 404, April.

Despite maximization of EW by utilizing **hot spots in the tropics**, the authors estimated implementation costs (combined capital and operational) for achieving an initial 50 ppm drawdown of atmospheric CO₂ are **\$60–600 trillion** for mining, grinding and transportation, assuming no technological innovation, with similar associated additional costs for distribution. These costs are detailed in the following tables. Good luck with ever getting that kind of funding.

Supplementary Table S10.	Estimated	combined	capital	and	operational	costs
associated with mining, grinding	g, transport	and spread	ing of ma	ateria	I from the air	. Cost
in US dollars (\$US) converted from Great British pounds (GBP) assuming an exchange						
rate of 0.63 GBP per \$US. This	s table has b	been adapte	d from	Renfo	orth et al.122.	

	\$US tonne ⁻¹	\$US tonne ⁻¹	
	lower	upper	
Excavation/drilling	0.79	0.79	
Grinding (comminution)	5.40	64.60	
National transport	8.57	9.21	
International transport	42.86	46.03	
Air-spreading	80 ª	155 ^b	
Total	162.50	325.83	

^a Taken from Wickström *et al.* Swedish Forest Agency¹²³ 10-year catchment liming project

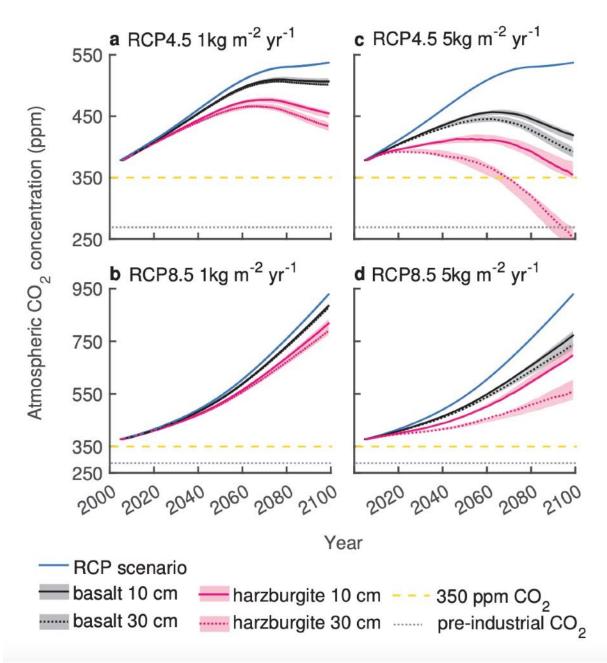
^b Estimate taken from whole-catchment lime application by aircraft reported in Donnelly et al.¹²⁴.

It is of note that the major expenses are international transport and air-spreading. If the ultramafic rocks can be obtained locally, and the expense of air-spreading cut by using drones, the costs could be as low as \$12 trillion, still a huge amount.

Application scenario	Initial 50 ppm CO ₂ drawdown						
	Year achieved	Rock required (Pg)	Rock prep. & transport Cost (Tn US\$)		Spreading costs Cost (Tn US\$)		
			lower	upper	lower	upper	
1 kg Harz. m ⁻² yr ⁻¹	2064	1,180	68	142	94	183	
5 kg Harz. m ⁻² yr ⁻¹	2034	2,900	167	350	232	449	
1 kg Basalt m ⁻² yr ⁻¹	2099	1,880	108	227	150	291	
5 kg Basalt m ⁻² yr ¹	2054	4,900	282	591	392	760	

Supplementary Table S11. For application in tropical weathering hotspots (20 Mkm²) under RCP8.5 – expenditure (trillions of US dollars) required for initial consumption of 50 ppm atmospheric CO_2 based on the tonnage of rock required.

Taylor et al (2015) also presented the following rather pessimistic figures. They stated they showed that using enhanced weathering scenarios covering **less than a third of tropical land could significantly drawdown atmospheric CO₂ and ameliorate ocean acidification by 2100.** The following diagram emphasizes the level of pessimism.



Two different RCP scenarios are illustrated. RCP 4.5 predicts a global temperature of 2.4° C with slowly declining emissions. With the application of 1 kg of climate rocks per square meter per year, the ppm of atmospheric CO₂ begins to decrease by 2060. If 5 kg per square meter per year is applied the ppm of CO₂ begins to decline by 2025. However, 5 kg of rock per square meter is an enormous amount of rock. With an RCP at 8.5 and a temperature of 4.3° C and rising emissions, despite placing 5 kg of rock per square meter, the ppm of CO₂ continues to rise.

This again illustrates the critical need for both the reduction of emissions (RPC 4.5) and NETs.

Particle Size. Particles less then 5 ums in size can be inhaled deep into the lungs while particles smaller than 1 um tend to be re-expelled (Jabbal et al, (2017). To avoid potential danger to workers appropriate masking would be required.

Reporting on EW/OAE in the Lay Press

In addition to the reports about EW/OAE in the peer reviewed scientific literature, as reviewed above, **there have been many articles in the general science, technical and lay press about the concept and virtues of EW/OAE**. The following is a listing of some of these: Ack (2022), American University (2020), Baez, J. 2019, Engineering Monitor (2021), Schuiling, O. (2007), BPH (2020), Farber, D (2020), Hance, J (2023), Johnson, B. (2022), Kersbergen, G, (2020), Okane, (2022). Jennifer L. (2022), Sandalow, D. et al (2021), Silverman, K.(2021), Temple, J. (2020), Whiting, T.(2022).

The following are some of the headlines: Temple, J. (2020). How green sand could capture billions of tons of carbon dioxide. Ack, B. (2022) How to Reverse the Ocean-Climate Crisis. Gallucci, M. (2022) Meet a startup that plans to use mining waste to capture carbon dioxide.

The disturbing aspect is that despite the widespread, very favorable coverage of EW/OAE, with very few exceptions, <u>there is still virtually nowhere in the world, including</u> the U.S., where ultramafic rocks are being mined and used to help combat global warming.

There were several important points made by these articles. They are as follows.

Ack, B. (2022) Human enterprise since the dawn of the industrial revolution has emitted about 2 trillion tons of CO₂ into Earth's atmosphere. This has resulted is a 50% increase in the amount of CO₂ in the atmosphere and a 30% increase in CO₂ in the upper layers of the ocean. This has resulted in both thermal and chemical stress on the ocean.

Thermal stress comes as the massive amounts of excess CO₂ put into the air which traps an enormous amount of energy from the sun that would otherwise have dissipated into space about 93% of all this excess heat is absorbed into the ocean. The quantity is staggering, calculated at about 14 zettajoules of heat every year. This is one joule with 21 zeros after it. **This is roughly** <u>equivalent to five Hiroshima type atomic bombs' worth of heat energy going into</u> <u>the ocean every second</u>. This means that, <u>every day, 432,000 atomic bombs' worth of excess</u> <u>heat energy enters the ocean</u>. Warmer ocean water holds less oxygen equivalent to about a 2% average decrease in dissolved oxygen throughout the ocean.

Warmer waters also lead to marine heat waves that decimate coral reefs; we have already lost more than half of the Earth's tropical coral reefs primarily due to heating and bleaching. In addition, warmer waters lead to large-scale migrations of fish stocks poleward. And warmer waters mean less Arctic Sea ice, which has functioned like a planetary air conditioning system for the world.

Chemical stress. As the ocean absorbs the excess CO₂, it becomes increasingly acidic. The ocean is now about **30% more acidic than it was in preindustrial times**. As a result, the ocean becomes less hospitable to all life that forms a shell, namely, many phytoplankton and zooplankton—the microscopic life forms that sit at the base of the food chain. As pointed out in the section on tipping points, phytoplankton sequester an amount of CO₂ equivalent to all the plants and trees on earth. Loss of phytoplankton would result in a loss of a massive CO₂ sink. Clearly the climate crisis is also an ocean crisis. This illustrates how important the different ocean-based NETs will be. Ack (2022), who is executive director and chief innovation officer for Ocean Visions pointed out that we desperately need to engage an ever-growing cadre of scientists, engineers, managers, environmentalists, businesses, investors, and others to tackle critical obstacles and pursue ocean as well as terrestrial NET technologies. We agree.

American University (2020) The long-term potential for enhanced mineralization is very large, both in terms of annual carbon removal and cumulative carbon sequestration. A recent expert assessment estimates that enhanced mineralization could be scaled up to capture 2–4 billion metric tons of CO₂ (GtCO₂) per year by 2050, with rates of more than 20 GtCO₂ per year theoretically possible by 2100. Estimates of the cumulative potential in this century range from 100 GtCO₂ to 367 GtCO₂. Cost estimates vary widely, from less than \$50 per ton of CO₂ sequestered to more than \$200 per ton.

The basic chemistry of EW is well understood, and the technology to mine, grind, and disperse rock is widely available. Research on enhanced mineralization as a form of carbon removal, however, remains in comparatively early stages, with much more work to be done to evaluate its efficacy and social and environmental sustainability.

Engineering Monitor (2021) reviewed some of the institutions and people currently conducting research on EW/OAE. These included Oxford Geoengineering Program led by Tim Kruger at Oxford University. The project Greenhouse Gas Removal by Enhanced Weathering (GGREW) aims to explore the feasibility of EW in oceans, assess different ways to accelerate the weathering process artificially and plans to conduct open-ocean trials in the Great Barrier Reef, Australia and in the Gulf of Aqaba, off the coast of Israel. Since 2008, Tim Kruger has been trying to market an OAE approach based on lime through his company Cquestrate, which received early-stage funding from Shell.

The Leverhulme Centre for Climate Change Mitigation (LC3M) is based at the University of Sheffield, UK. It is directed by David Beerling and was founded in 2016 to conduct research on EW on croplands as a potential strategy for increasing field yields while removing CO_2 from the atmosphere. The research activities also include field trials at farming sites, applying 50 tons of mined and crushed basalt per hectare per year, to test EW in different agricultural environments. The trials are conducted on farms in Australia, Malaysia, and the USA with various crops, including oil palm, sugar cane and soy.

In the Netherlands, **Olaf Schuiling** conducted lab-based research on EW with olivinerich rocks at Utrecht University. He founded the **Smart Stones Foundation (formerly The Olivine Foundation)** in 2009 to promote and commercialize olivine applications for CO₂ removal and conducted small-scale trials. Schuiling's research contributed to the founding of the Dutch companies **Green Sand** and **Green Minerals**, both trying to commercialize EW with olivine-rich rocks.

In Northern America, researchers at the University of Guelph, Ontario, test EW with the calcium silicate rock called **wollastonite**, in pot trials with beans and corn. The Californiabased **Project Vesta**, founded by **Eric Matzner**, aims to set up a project for testing EW with olivine-rich rocks on beaches. Some down sides of EW/OAE were discussed. Huge amounts of rocks would need to be mined, **comparable to present day global coal mining**. Such massive mining operations would increase exponentially the devastating effects of mining on poor communities around the world, as well as increase the significant adverse environmental impacts. EW requires these big quantities of rocks to be milled, transported, and dispersed, which further increases the CO₂ and environmental footprint of EW. **These considerations help to emphasize the advantages of heOAE which requires no climate rocks and no burial of CO₂.**

Baez, J. (2019) mentioned some relevant observations such as 140 grams of olivine will sequester 176 grams of CO_2 with the help of 72 grams of rain or seawater. A kilogram of serpentine can sequester about two-thirds of a kilogram of CO_2 . There is approximately an order of magnitude more serpentine than olivine.

Farber, D. (2020) reports that for EW of cropland, David Beerling has largely switched to ground **basalt**. Basalt is rich in pyroxene, a blocky, dark mineral that, like olivine, weathers quickly but **does not contain toxic heavy metals**. The downside is that olivine weathers faster than basalt. Also, basalt is ineffective for use in OAE.

A bit of history. Chemical weathering, first described by the French geochemist and metallurgist **J.J. Ebelman in 1845**. It was brought to broad scientific attention when Nobel Laureate **Harold Urey**, a University of Chicago geochemist, reported it in Proceedings of the National Academy of Sciences in 1952. **Walter Seifritz**, a little-known physicist, and nuclear engineer at Switzerland's Paul Scherrer Institute, penned a letter to Nature suggesting, "It would be advantageous if there were an abundant mineral to which CO₂ could be bound chemically via an exothermic reaction to form a stable, permanent substance." He suggested that silicate minerals would serve that purpose well, and that an industrialized process based on chemical weathering could remove CO₂ from the atmosphere. **Beerling stated that "The idea lay dormant until people started to realize that we need negative emissions to get us out of trouble."** In 2006, Dutch geochemist **Olaf Schuiling** of the University of Utrecht proposed the large-scale use of olivine, a green silicate mineral found in basalt, peridotite, and other common igneous rocks, to draw down carbon dioxide.

Steve Long, a professor of crop sciences and plant biology at the University of Illinois, Urbana-Champaign, took up Beerling's idea of spreading basalt on cropland. He stated that in the Midwest, there were 90 million hectares of corn and soybean land, and all those farms are equipped with **lime spreaders**. Kantola, Long, and several other colleagues, Carl Bernacchi and Evan DeLuci, have been applying ground basalt to half of a 50-acre section of the **Energy Farm**, using the fields in the other half as a control. They've monitored a wide variety of soil, plant, and atmospheric parameters to answer questions about carbon dioxide drawdown and how the basalt affects the soil and crops that grow in it. The Illinois field trials are now in their fourth year, and the researchers plan to report later this year how the treatment affects CO₂ uptake and how the soil and crops respond, both above and below ground. One benefit was that corn and miscanthus fields reduced nitrous oxide emissions 16 percent and 9 percent.

Researchers at the **University of Guelph** in Ontario showed that ground **wollastonite**, another common rock rich in silicate minerals, underwent weathering in soil, drew down significant amounts of carbon dioxide, and improved the growth of soybeans and alfalfa. It also contains very little nickel or chromium.

In a recent modeling study, University of Salzburg researchers showed that basalt had to be ground to fine, silt-like particles, which can take so much energy it can cancel out the CO_2 drawdown benefits from weathering. The use of solar or wind energy for grinding, could negate that.

Hance, J (2023) Ocean Visions has been evaluating OAE grant proposals in partnership with the Palo Alto California-based NGO Additional Ventures. Co-founded by a former Meta executive, Mike Schroepfer, Additional Ventures has put aside \$100 million for OAE research and development. The two NGOs are currently evaluating proposals for two different grants. The first will support projects to develop prototypes of equipment to produce or deliver minerals, with funding ranging from \$750,000 to \$1.5 million; the second will support projects to explore how OAE could be done safely and effectively, with minimum funding of \$10 million. They'll announce the grant recipients later in 2023 and research will take up to five years.

Kersbergen, G, (2020) Natural weathering speed is actually quite high, due to **biotic factors** like microorganisms, lichen, ants, vascular plants, and lugworms (Schuiling, 2017). Many factors have an impact on the weathering rate of olivine. It is not easy to answer to what degree the organisms and the abiotic factors affect the weathering process of olivine because a lot of factors influence the weathering process and they are often very complex (Brady et al., 1999). The factors are often coupled with one another, which makes it hard to investigate one factor in isolation.

Science Daily (2018) claimed more than 3 billion tons of basalt are needed to sequester one billion tons of CO₂, a mindboggling amount equal to almost half of the current global coal production.

Sandalow, D et al (2021) EW offers gigaton-scale capacity to capture and permanently store CO₂. The main advantages of EW are the simplicity of the approach, consistency with current mining and agricultural practices, and co-benefits that may include improved soil fertility in some areas. The main challenges of EW are the lack of widely accepted methodologies for determining CO_2 removal rates and concerns about environmental risks from accumulation of metals, including nickel and chromium.

Silverman, K. (2021) During the Green Revolution, Brazil's 180-million-hectare Cerrado eco-region was unfit for farming due to naturally acidic soil. To change this, over 15 million tons of limestone were spread over the fields from the 1960s-1990s at about five tons per hectare. Now the region is a major contributor to Brazil's soybean production while still being the predominant national source of cattle. This showed the technical potential of such a practice and the possibilities - for restoration or expansion - that it unlocks for producers.

Gallucci, M. (2022) Travertine Technologies has backing from Stripe's carbon-removal fund for a novel system to store CO_2 in discarded rocks and help clean up the mining industry. Travertine was one of six carbon-removal companies to receive a combined \$2.4 million in Frontier's first purchase round. Two of the other startups — Lithos Carbon and Calcite-Origen — are also working with minerals, though neither is focused on mine waste. AspiraDAC and

RepAir are both building systems that capture carbon directly from the air, while **Living Carbon** is attempting to sequester CO₂ using algae.

"We are always looking for more pathways [for carbon removal] because doing this at scale is so challenging," said Scott Litzelman, the program lead for **Stripe's Frontier Fund**. "And it's important to show that there is private-sector demand for these services."

Temple, J (2020) Project Vesta plans to spread a green volcanic mineral known as olivine, ground down to the size of sand particles, across a beach. The waves will further break down the highly reactive material, accelerating a series of chemical reactions that pull the greenhouse gas out of the air and lock it up in the shells and skeletons of mollusks and corals.

The Leverhulme Centre for Climate Change Mitigation, in Sheffield, England, is running field trials at the University of Illinois at Urbana-Champaign to assess whether basalt rock dust added to corn and soy fields could act as both a fertilizer and a means of drawing down carbon dioxide.

Perhaps Not Hopeless

Despite the many negative opinions shown above, in the **Negative Thinking About EW Negative Emissions Technology** section, The Energy Futures Initiative (2020) article entitled: *Rock Solid: Harnessing Mineralization for Large-Scale Carbon Management*, makes the following key statements.

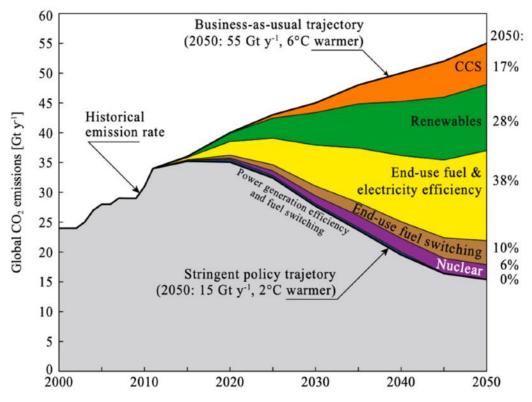
1. Carbon mineralization (EW) provides a pathway to near permanent isolation of carbon dioxide (CO_2) from the environment.

2. Technological enhancements can expand and accelerate natural carbon mineralization, making it feasible to achieve gigaton (Gt) scale CO₂ removal (CDR).

3. Carbon mineralization has several co-benefits that enhance its attractiveness. They make several recommendations.

4. Each pathway has the scaling potential to achieve Gt-scale CDR within a cost range of less than \$100 per ton of CO₂.

5. Wedges Importantly - we don't have to do it all with EW and OAE, eOAE and heOAE.



IEA. Energy Technology Perspectives (2014), International Energy Agency

This diagram from IEA illustrates the **concept of multiple wedges**. Renewables, electricity efficiency, and nuclear will all be needed in addition to EW/OAE/eOAE and heOAE. However, of these only *in situ* CCS and EW/OAE/eOAE and heOAE can actually remove CO_2 from the atmosphere and this wedge will need to account for much more than 17%, **but not 100% as assumed in the more negative comments above**.

We are not recommending that *in situ*, EW and the 3 OAEs are the only NETs to get to many gigatons of CO₂ sequestration. **DACS can still be used**, **but it should not be depended upon to reach the 10 - 20 gigaton/yr level. In addition, more government funds need to be spent on getting EW and the OAEs up and running.**

In addition, <u>All the minor NETs, Cobo et al (2022), should also be utilized.</u> <u>Together they could contribute multiple gigatons per year of sequestered CO₂, a not insignificant part of the total.</u> Of interest, in its sixth assessment report, released in March 2023, the Intergovernmental Panel on Climate Change (IPCC) pointed out that the many other NETs such as "biological CDR methods like reforestation, improved forest management, soil carbon sequestration, peatland restoration and coastal blue carbon management can enhance biodiversity and ecosystem functions, employment and local livelihoods." They preferred these methods over DACS.

It has been suggested that to get to zero carbon emissions in the U.S we would need 78 million roof top solar arrays, 485,000 wind turbines, 9,000 solar power plants and massive energy storage. From this point of view, EW and the 3 OAEs seem easy.

Are Heavy Metals a Problem for EW and OAE?

This section reviews several papers that specifically address the question of whether heavy metals are a significant problem for EW, OAE and eOAE. This is relevant because one of the most frequently cited concerns about EW/OAE are related to heavy metals, especially nickel and cadmium. There are basically seven important questions.

- 1. How is nickel and cadmium bound to climate rocks?
- 2. How much nickel and cadmium are in climate rocks?
- 3. How much nickel and cadmium are already in soils?
- 4. After EW does Ni and Cd get into the soil?
- 5. Is it a Problem for EW?
- 6. Is it a Problem for OAE?
- 7. What are some ways to work around the problem?

1. How is nickel and cadmium bound to climate rocks? This is relevant to the question of whether it would be easy to remove, especially nickel, from pulverized rocks before using them for EW/OAE/eOAE. Is the nickel in a form that can be easily separated from olivine or is it chemically bound?

Santos, et al (2015) showed that nickel can replace magnesium in olivine's magnesium silicate matrix forming a magnesium-nickel silicate $(Mg, Ni)_2SiO_4$ called **liebenbergite or nickel-olivine**. This replacement is possible due to certain similarities of nickel and magnesium in the silicate structure. Their ionic radii are similar (Mg = 0.66 Å; Ni = 0.69 Å), their valences are the same (Mg²⁺, Ni²⁺), and they both belong to the same orthorhombic crystal system. It was best extracted from olivine in a fully carbonated form, (Mg,Fe)CO₃) using **different acids**. While nickel appeared to be dispersed throughout the material in some cases highly concentrated nickel was also found in a few small particles and the few chromium-rich particles.

Sato, H. (1977) By contrast Sato, (1977) stated that the Ni content of basaltic magmas is due to the presence of NiO. In this case, since Ni is present as a separate compound that was not chemically attached to basalt, it should be easier to extract. However, the level of Ni in basalt is sufficiently low such that for basalt it not an issue (see below).

2. How much nickel and cadmium are in the climate rocks? The amount of nickel and cadmium in olivine is variable and depends on the ore's origin. Vink et al (2022) reported the following figures: Nickel concentrations in Norwegian and Spanish olivine were 2,110 and 1,301 mg/kg while in Canadian Wollastonite it was only 20.6 mg/kg. The chromium concentrations in the two olivines were 2,201 and 2,281 mg/kg while in Canadian Wollastonite it was only 24.1 mg/kg. Sato (1977) reported the concentration of Ni in basalt as 30 to 50 mg/kg. This is the reason many researchers have preferred to use basalt for EW.

3. How much nickel and cadmium are already in soils? An extensive review of heavy metals in soils is found, not surprisingly, in the book *Heavy Metals in Soils*, edited by Brian J. Alloway. Chapter 11 Chromium and Nickel by C. Gonnella and G. Renella, is especially relevant.

Nickel. Total Ni concentrations of up to 7,000 mg/kg can be found in 'ultramafic' soils originating from igneous ultramafic rock. High concentrations of about 2,000 mg/kg of both Ni

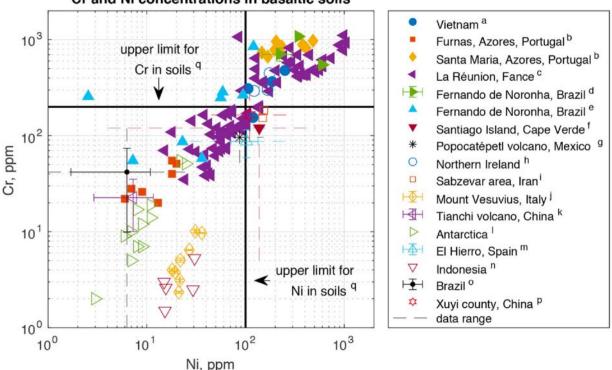
and Cr can be found in the so-called "serpentine" soils. Soil toxicity threshold concentrations for Ni are commonly reported to be in the order of less than 100 mg/kg. In view of this, the maximum admissible Ni concentration established for agricultural soils based on the 86/278/EEC directive are **30 mg/kg for acidic soils and 75 mg/kg for neutral alkaline soils**.

Chromium. Chromium presents an average concentration of 100 mg/ kg in the Earth's crust whereas the concentration range in soil is between 1 and 3,000 mg/kg. The total Cr concentration in soil varies from 0.5 to 250 mg/kg with average values varying between 40 and 70 mg/kg. Chromium is mainly associated with mafic and ultramafic rocks in which it can reach values of 3,000 mg/kg. Even higher Cr concentrations, up to 10,000 mg/kg, are present in soils formed from mafic and volcanic rocks. These finding are important because they indicate that sometimes the problem is not with EW but with the soils themselves.

The following two studies show the levels of heavy metals in both the soil and the rocks.

Suhrhoff, T J (2022) There is a large variability of heavy metal concentrations in basaltic and ultramafic soils. Hence, to minimize environmental risks of enhanced weathering, basalts with low heavy metal concentrations should be favored.

The following diagram illustrates the wide variability of Ni and Cr in various soils.

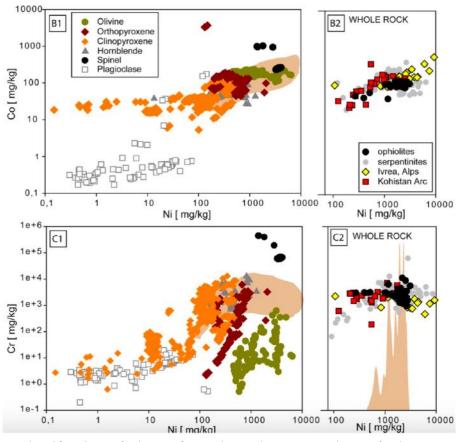


Cr and Ni concentrations in basaltic soils

Chromium and Ni concentrations in soils derived from basaltic rocks. The chosen acceptable limits for agricultural soils are representative of average limits throughout the EU.

This shows that many times the levels of Ni and Cr in climate rocks is not a problem.

Kierczak, J. et. al. (2021) As Suhrhoff (2022) reported the variation in Cr, Ni and Co content for a range of basaltic soils, Kierczak et al (2022) have done the same for **ultramafic** soils and rocks.



Classification of ultramafic rocks and concentrations of Ni, Cr, and Co in whole rocks and major ultramafic minerals.

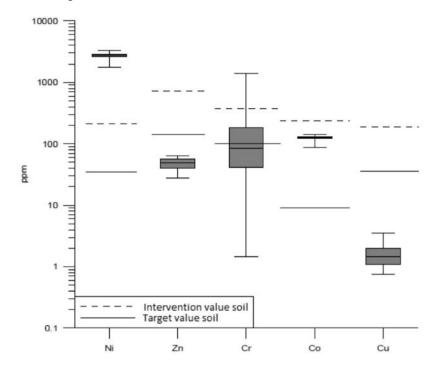
For the upper limit of safe levels, they used median world Regulatory Guidance Values - RGVs). These were **110 mg/kg for Ni**, **250 mg/kg for Cr** and 50 mg/kg for Co.

4. After EW does Ni and Cd get into the soil?

Boogaard, S. (2020). The aim of this study was to investigate whether olivine can be effectively implemented within environmental safety boundaries for the Knowledge Mile Park in Amsterdam. There were three scenarios to sequester atmospheric CO_2 - tree sand that trees grow in green rooftop substrate, and footpath substrate. Using an Olivine Weathering and CO_2 Sequestration model and PNEC-pro V6, the dissolution and CO_2 sequestration rate of olivine were examined and the released nickel concentration with the effects on various plant and aquatic species was analyzed. Green rooftop substrate was identified as the most effective scenario in terms of the magnitude of CO_2 binding.

High amounts of nickel (Ni) are released during the weathering of olivine. Due to its unknown environmental hazard, the released nickel concentration is one of the primary bottlenecks for the practical implementation of olivine. **This limit is specific for different areas** with an average of 35 mg nickel per kilogram soil in the Netherlands. Besides, the environmental quality standard (Milieukwaliteitsnorm, MKN) for surface water applies a limit of 34 µg nickel per liter.

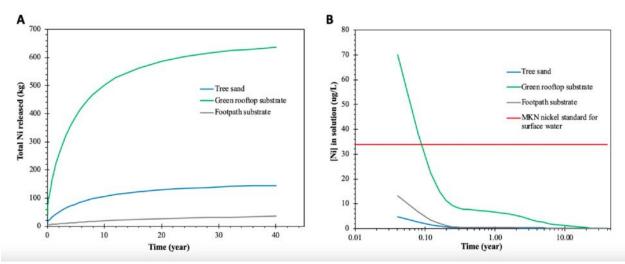
To prevent the exceeding of these limits, the Dutch fertilizer law (Meststoffenwet) states that, when implementing in agriculture or as a substrate in the 'green space', a magnesium-rich fertilizer is allowed to have a maximum nickel concentration of 800 mg Ni/kg. Since the average nickel concentration in olivine is approximately 3,000 mg Ni/kg, this target is exceeded, making olivine not suited for implementation in these areas. This is illustrated in the following figure.



Metal concentrations of 75 olivine samples of different origin with target and intervention values of the soil, according to the Dutch law, as reference.

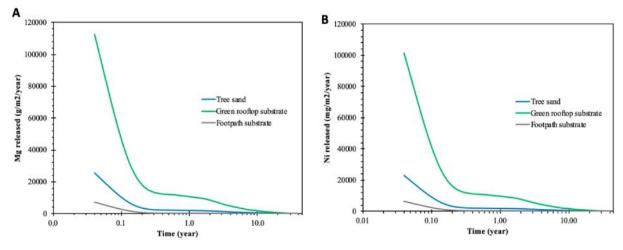
This shows that the levels of Ni (nickel) and Co (cobalt) in olivine exceed recommended safety levels while the levels of Zn (zinc), over half of (chromium) cases, and Cu (copper) do not.

The following figure shows the amount of CO₂ sequestered over time.



Output of the specification of nickel release of the OWCS weathering module. Depicted is (A) the total amount of nickel released (kg) by olivine over time and (B) the nickel concentration in solution (μ g/L) by olivine over time with the environmental quality standard (Milieukwaliteitsnorm, MKN) of 34 μ g/L for surface water (red)

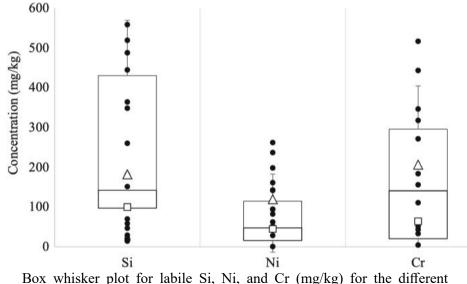
The following figures shows that the rate of CO₂ sequestration as measured by Mg release (A) and the rates of Ni released (B) over time are comparable.



(A) the amount of released magnesium (g/m2/year) by olivine over time and(B) the amount of released nickel (mg/m2/year) by olivine over time.

This is consistent with the Santo et al (2015) report that the Ni is bound as $(Mg, Ni)_2SiO_4$. One caveat, less than 5% of the particles were 1 um or less in size and 80% were 10 um or greater.

Haque, F. et al, (2020) provided an analysis of the risks associated with the release into the soil of Si, Ni and Cr from alkaline silicate minerals such as olivine. This was to evaluate its potential to be applied as a soil amendment for enhanced weathering. The following diagram summarizes these results.



Box whisker plot for labile Si, Ni, and Cr (mg/kg) for the different sampling sites in the literature. (Δ = mean, \Box = SQG E values). SQE is the Soil Quality guideline value for the Environmental health of the heavy metals found in the soil in mg/kg.

Enhanced weathering of silicate minerals was associated with the release of heavy metals such as Ni and Cr, depending on the composition of the parent rock. The above diagram shows that while in some case the application of Ca and Mg silicates to the soil does not result in amounts of Ni or Cr that exceed safe levels (boxes), while in some cases it does exceed such levels. The presence of Ni and Cr can be beneficial if their soil concentration does not exceed these toxic levels.

Pastures grown over basaltic fines accumulated 2.17 mg/kg as bioavailable Ni (Néel et al. 2007), whereas pastures grown on serpentine-derived soils accumulated higher levels of bioavailable Ni (11.1–39.3 mg/kg) (Miranda et al. 2009). Fernandez et al. (1999) reported Ni content of 12–34 mg/kg in the foliage of various crops grown over serpentine-treated soils. These can result in high Ni accumulation in kidney tissue of grazing cattle (Miranda et al. 2009). Alkaline silicate minerals are also associated with the release of Si, which is a beneficial element in plant nutrition.

Flipkens, G. et al. (2021) derived a guideline for coastal olivine dispersal based on existing marine environmental quality standards (EQS) for Ni and Cr. The results showed that benthic biota (sea bottom) are at the highest risk when olivine and its associated trace metals are mixed in the surface sediment. Specifically, 0.059–1.4 kg of olivine/m² of seabed could be supplied without posing risks for benthic biota. Accordingly, globally coastal EW could safely sequester only 0.51–37 Gt of CO₂ in the 21st century. Based on current EQS, they conclude that adverse environmental impacts from Ni and Cr release could reduce the applicability of olivine in coastal EW.

In summary, in some cases the level of Ni in the soil after the application of olivine for EW exceeds recommended safe levels while in other cases it does not.

5. Is it a Problem for EW?

Lenferink, J and Knops, P. (2018) developed a model that calculates the weathering rate of olivine, as a function of time, pH, grainsize and dosage, and thereby also the CO₂ sequestration amount and speed. The model includes risk modules for Ni in terrestrial and aquatic systems The model was validated and used to predict CO₂ sequestration amounts for several large-scale olivine applications in the Netherlands.

The presence of Ni is one of the main bottlenecks when it comes to practical applications of olivine, as it becomes toxic to plants and animals in higher concentrations. They linked the weathering rate of olivine to the amount of Ni released in the soil solution. Their simulations indicate that the release of Ni has no negative effect on the ecosystem, therefore the possibilities for olivine application and CO₂ sequestration are endless. This is clearly an optimistic assessment!

Beerling et al (2018) performed a synthesis by of published chemical analyses which indicated that olivine-rich ultramafic rocks contain relatively high concentrations of chromium (Cr) or nickel (Ni) or both. Weathering experiments revealed fast release of bioavailable Ni from olivine, and suppression of plant calcium uptake, because of competition with magnesium. Experimental work with a soil-columns dosed with olivine suggested accumulation of Ni and Cr in the soil profile.

Adrees, M. et al (2015) Silicon (Si) is the second most abundant element in the soil. Si can stimulate plant growth and alleviate various stresses, including heavy metal stress. The key mechanisms evoked include reduced metal uptake, chelation, and stimulation of antioxidant systems in plants, complexation and coprecipitation of toxic metals with Si in different plant parts, compartmentation and structural alterations in plants and regulation of the expression of metal transport genes. These features should provide some protection against the effects of heavy metals.

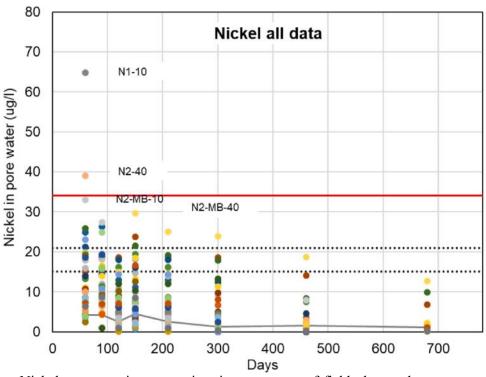
Vink, J. et al (2022) A two-year field experiment was conducted in the Netherlands to study mineral weathering rates under various conditions. Variables were - mineral source (Norwegian and Spanish olivine, Canadian wollastonite), type of application (on-top versus mixed-in), availability of moisture (rain-fed versus wet), and effect of vegetation (planted versus non-planted). All field plots contained mesocosms with similar treatments for mass-balancing. Pore water was sampled periodically over various depths, and different chemical extractions were applied to the soil. The numerical model, OWCS, based on the shrinking core principle, was calibrated with data obtained from the field experiments. A separate risk assessment module for nickel was developed and incorporated in the model.

The results showed that 6 to 8.5 percent of the initial mineral dose was dissolved after two years. Applying the Shrinking Core Model to each grain size, the dissolution over time could be calculated accurately. Of the smallest grain fraction ($<2\mu$ m), 100 % of the mass is dissolved in two years. In the same period, 42.9 % of the fraction < 8 µm is dissolved. The larger fractions show decreasing dissolved portions respectively. Modelled and measured values show a good agreement. The grain size distribution of the ground minerals played a decisive role in weathering rates.

Nickel concentrations in Norwegian and Spanish olivine were 2,110 and 1,301 mg/kg while in Canadian Wollastonite it was only 20.6 mg/kg. The chromium concentrations in

the two olivines were 2,201 and 2,281 mg/kg while in Canadian Wollastonite it was only 24.1 mg/kg. The particle sizes were quite large mostly ranging from 300 to 6,000 ums for the olivines and less than 500 ums for wollastonite. The experiments were carried out in field plots and mesocosms.

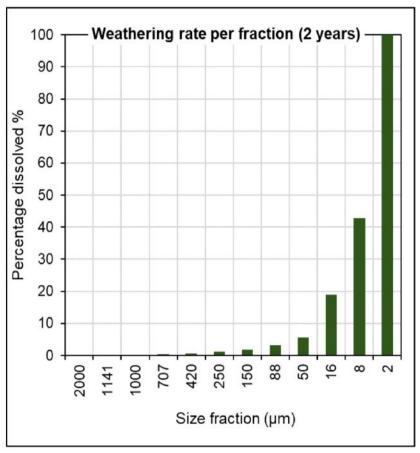
Nickel concentrations in pore waters are elevated compared to the reference plot. **However, 96 % of all Ni measurements are below the analytical upper reporting limit**. Only two measurements (Norwegian olivine source) exceed the generic quality standards but only shortly after application. In the first period of weathering, **most nickel is released from the ultrafine fraction**. In all cases, the calculated No-effect concentration (PNEC) for nickel is larger than its measured value in pore water and are (far) below the risk characterization ratio (RCR < 1). This is a **strong indication that no chronic toxic risks of nickel release are to be expected for the concentrations observed during the experiment**. These results are shown in the following figure.



Nickel concentrations over time in pore water of field plots and mesocosms. Dotted lines are upper and lower analytical reporting limits. The Red line is the WFD-environmental quality standard of nickel in surface water.

The five highest Ni-concentrations recorded are all from plots with Norwegian olivine. Norwegian olivine has a higher nickel content than the Spanish olivine (2110 versus 1301 mg/kg), which becomes available upon weathering.

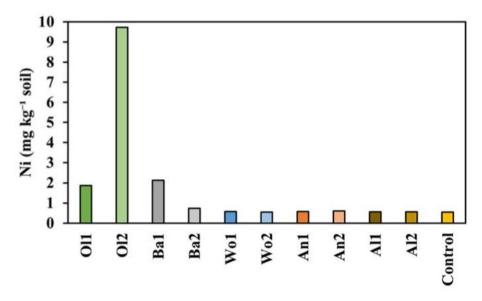
As shown in the following diagram, these studies once again showed a strong dependence between weathering rate and particle size.



Weathering rate versus particle size.

te Pas et al (2023) compared the enhanced weathering potential of olivine (Mg₂SiO₄), basalt, wollastonite (CaSiO₃), and two minerals that are novel in this context, anorthite (CaAl₂ Si₂O₈) and albite (NaAlSi₃O₈). Their results showed comparatively high CO₂ capture by wollastonite and olivine weathering. Furthermore, CO₂ capture per m² specific surface area indicated potential for enhanced anorthite and albite weathering. All silicates generally improved soil quality, with soil nickel contents remaining below contamination limits. However, nickel concentrations in leachates from olivine-amended soils exceeded the groundwater threshold value, stressing the importance of monitoring nickel leaching. They found a relatively high enhanced weathering potential for wollastonite, while the potential for olivine may be constrained by nickel leaching. The promising results for anorthite and albite indicate the need to further quantify their enhanced weathering potential.

The following figure shows the nickel release by different rocks.



Geochemically reactive soil Ni concentrations at the end of the experiment, based on 0.43 M HNO₃ extraction.

The fact that wollastonite showed high CO₂ capture, but low release of nickel suggests that wollastonite would be ideal for EW. However, the estimated world production of crude wollastonite ore was 1,200,000 tons in 2021. World reserves of wollastonite are estimated to exceed 100 million tons, though some existing deposits have not been surveyed. Major producers of wollastonite include China, India, the United States, Mexico, and Finland. Even if all of this was mined, and 1 ton of wollastonite sequestered 1 ton of CO₂, this would only account for one-tenth of a gigaton. By contrast, olivine is one of the earth's most common minerals by volume. This diagram also showed that two different treatments of olivine produced markedly results for nickel.

Vienne, A. et al (2022) using a 99-day mesocosm experiment with the Irish potato, growing on alkaline soil found that with the addition of 50 t basalt/ha, nickel levels remained below regulatory environmental quality standards. This consistent with the fact that basalts contain significantly less nickel than olivine.

Renford, et al (2015). Experimental work with a soil-columns dosed with olivine suggested accumulation of Ni and Cr in the soil profile. From the results of this study, there was elevated Cr in five of the solution samples from the olivine column, the remaining samples showed no difference compared to the control. Ni was measured but was below the detection limit in all of the effluent solutions.

Nickel in Different Plants Generally, the nickel concentration in plants varies between 0.1 and 5 mg/kg depending on the season, the amount of nickel present in the soil and specific plant species and parts. Furthermore, the critical toxicity values of different plant species also show a high variability with more than 10 mg/kg for sensitive species, 50 mg/kg for intermediate tolerable species and 1000 mg/kg in nickel hyperaccumulator plants (IPNI, n.d.). (Boogaard, S. (2020).

Field observations in natural enriched Ni-areas in Europe, indicate very limited adverse effects on groundwater or plant life (Tarvainen et al., 2005)

Schuiling and Krijgsman (2006) stated that if we spread one ton of dunite, it contains 1.4 kg of nickel. A hectare of soil with an average soil depth of 0.5 m weighs approximately 10,000 tons. This means that we add only 0.14 ppm of nickel to such soils every 30 years. As nickel is the most abundant potential contaminant in olivine-rich rocks, it appears that heavy metal pollution is not an issue with dunite applications and that there are no adverse environmental consequences if we substitute liming by the application of olivine. The second commonest trace metal in ultramafic rocks like dunite is chromium, but most of it is tightly bound in very insoluble chromite grains and will not be bioavailable.

These studies range from claiming the Ni poses no problem for EW, to occasionally it may cause a moderate problem. Cr appears to be less of a problem.

6. Is it a Problem for OAE?

The impact of increased nickel flux on marine ecosystems is a matter of potential concern and is summarized on the Web site of the UK Marine Special Areas of Conservation (http://www.ukmarinesac.org. uk/) and established for the UK at a chronic concentration of the ecotoxicology of nickel in marine organisms and **0.25 \mu mol/L**. Nickel toxicity has been reported in a number of cases: negative effects on spawning in mysiid shrimps at 2.4 μ mol/, DNA damage with associated physiological and cytotoxic effects in the blue mussel *Mytilus edulis* at 0.3 μ mol/L, disrupting ionoregulatory functions in the green crab *Carcinus maenas* between 8.5 and 51 μ mol/L in very low-salinity seawater (0.006 PSU), and organ oxidative stress in the killifish *Fundulus heteroclitus*.

Nishimura (1968) showed that the atomic ratio of Ni/Mg decreases regularly with decrease in magnesium content of olivine.

J. Guo: Investigating the effect of nickel concentration on phytoplankton growth to inform the assessment of ocean alkalinity enhancement. Enhanced Weathering Conference (2022). He concluded that: a) The Ni sensitivity is species specific. b) The Ni tolerances of 11 tested marine species were surprisingly high. c) More Ni impacts in coastal regions than in the open oceans. d) Applications of OAE with Ni-rich minerals may be safer in regions with high organic ligand and low urea concentrations.

7. If are there ways to work around it?

There are several potential ways to ameliorate the effect of heavy metals on EW and OAE. These include the following.

a) Use ultramafic rocks that have lower amounts of heavy metals. The above review shows that there is a wide range in the content of Ni and Cr in olivine from different sources. If deposits with relatively low levels of Ni and Cr can be identified these should be the preferred source of rocks for EW and OAE. While basalt is not suitable for OAE there is a widespread use of basalts for EW because of their much lower level of Ni and Cr.

b) Do preliminary testing. Before beginning any field-scale application of olivine, either for EW or OAE, there should be field trials in quasi-contained conditions, such as mesocosm setups. This should include testing of the soil before applying the rocks. If the soils have low levels of Ni and Cd, they could tolerate EW better. It the level is already above toxic levels EW should be done elsewhere. A reviewed, there are huge areas of non-cropland land where the issue of Ni and Cd is less critical.

c) Use of nickel sequestering plants.

Olaf Schuiling (2018) demonstrated that by planting plants that are **nickel hyper accumulators**, such as those in the *Alyssum* family, in the same ground that is covered with olivine, at the end of the growing season the plants can be harvested by cutting them close to the ground. When these plants are burned the ash contains about 10% nickel, which is higher than the richest nickel ores. This is a very environmentally friendly way to mine nickel and can provide an income stream to help cover the costs of EW. The *Alyssum* can then re-grow for the next season with a new spread of olivine.

Surhoff (2022) listed a number of nickel accumulating plants, including *Alyssum*. The judicious planting to these plants could eliminate toxicity issues.

d) Remove Heavy Metals from Olivine and other rocks used for EW/OAE

Turri et al (2019) proposed removing nickel from olivine using **ion exchange** techniques. However, the need for the use of acids would make scaling up the process very difficult. It was recommended that further research might identify better ion exchange resins for this purpose. These include zeolites, bio-zeolites, maltose, and Lignocellulose/Montmorillonite Nanocomposite.

The **lignocellulose/montmorillonite nanocomposite** is especially intriguing. It is inexpensive and its maximum adsorption capacity of Ni(II) reached 94.86 mg/g at an initial Ni(II) concentration of 0.0032 mol/L, a solution pH of 6.8, an adsorption temperature of 70°C, and adsorption time of 40 min. One advantage is that it can be regenerated with HCl, one of the biproducts of electrolysis.

Bach et al, (2019) recommended the possibility of **removing heavy metals by electrolysis prior to placement in the ocean**. This could be incorporated into the above proposals to develop ships using solar and wind power and electrolysis for OAE. Several other recent studies suggest that electrokinetic techniques might be useful in removing heavy metals from climate rocks (He et al, 2018; Normile, 2022; Wang et al, 2022; Vocciante, et al 2021)

Olaf Schuiling suggested chromium can be recovered from pulverized olivine using shake tables or Humprey spirals. The recovered chromite also has some economic value. Using these approaches, it may be possible to remove most of the heavy metals from olivine before spreading it on the ground.

e) Not an Issue with heOAE. One of the advantages of heOAE is that since no climate rocks are added to the ocean, heavy metals is not a problem. The procedure uses electricity to rearrange the chemical composition of seawater without adding anything.

f) Not an issue with eOAE. Heavy metal contamination should also not be a problem with eOAE since several authors have suggested the during electrolysis it should be possible to remove heavy metal contamination.

g) Also, not a problem for OAE. As reviewed above (pages 192 -195) Fakhraee et al (2020, 2023) have shown that olivine (and basalt) are much inferior to CaO, MgO and Mg(OH)₂ for OAE. Thus, if olivine is not used for OAE the problem of heavy metals disappears. While Mg(OH)₂ can be made from olivine, it should not be a problem to remove any heavy metals in the process.

These considerations indicate that concerns about heavy metals should not be a contra-indication to the use of EW, OAE, eOAE and heOAE.

Olivine in Cement

There is one use of olivine where moderate amounts of heavy metals are not an issue. Shanks et al (2024) described a novel process that produces amorphous silica and nesquehonite (MgCO3·3H2O) from the olivine (Mg, Fe)2·SiO4). The amorphous silica forms a supplementary cementitious material for use in concrete. The formation of nesquehonite sequesters carbon making the overall process carbon negative. A report on this paper stated that with 35% olivine produced a carbon neutral cement while with 40% or more olivine made the cement carbon negative (New Scientist May 11-17, 2024, p19). This provides a second reason to begin mining olivine.

A Drone Program for Climate Based Non-profits

Exclusive of land for agriculture there are huge areas of other land including mountains, forests, shrubland, grasslands and pasture, wetlands, and others. The nature of both the mountains and these areas suggests that finely ground climate rocks would need to be spread by air. However, planes are very expensive, a trained crew is required, and the planes would themselves produce a lot of CO₂ exhaust, partially defeating the purpose. There is another option that **climate clubs could easily afford - drones**. Drones are not expensive, and they do not require a trained crew. Since they are electric, they do not spew CO₂ into the air. A special federal or state agency could monitor the program to ensure permissions and parcel different areas to different groups to avoid duplication.

There are many companies making commercial drones for sale. Some even specialize in agriculture use for spraying or seeding. The following is one example.

AIRBORN AGRO A downward facing radar keeps the drone at the right height.



It has a large holding tank with a 60-liter capacity. Once the mining of climate rocks has begun, millions of tons should be made available to interested NGOs and non-profits throughout the country for this **Drone Program**. The finely ground rocks could be sprayed as a slurry. Those Climate Clubs that wish to actively participate in the drone program can research the different models for themselves. Such a **Drone Program**, run by many different NGOs and non-profits, could reach gigaton levels of CO₂ sequestered.

DACS vs EH - Another Advantage of EH.

In addition to being safer than DACS, EH has an additional significant advantage. While DACS is done by a few companies with multimillion dollar investments in equipment, once the ground olivine is made available by the government or private industry, individuals can participate in the above-described drone program at a fraction of the cost of a car. As global warming gets progressively worse and affecting almost everyone on the planet, millions of individuals could be incentivized to participate in the drone program. During WWII in the US there were over 20 million victory gardens. This new world war against global warming could eventually enlist may times that number in the US and worldwide. This would also provide a very simple way for wealthy citizens to become involved by helping to subsidize the cost and distribution of the ground climate rocks for use by individual citizens.

NETs In Conclusion: Cobo et al (2022)

Cobo et al (2022) reviewed **36 different NET configurations**. The six most promising. were forestation, Soil Carbon Sequestration (SCS), **enhanced weathering (EW) with olivine**, and three modalities of Direct Air Carbon Capture and Storage (DACCS). In their Table 2. they provided estimates of the maximum number of gigatons of CO₂ removed per year for 28 different types of NET. At **95 Gt/year EW with olivine was the highest of all NETs listed by a wide margin**. All the others ranged from 0.006 to 13 Gt/yr. While this table contained no estimates for the six different types of DACS, a goal for several companies is one megaton of sequestration/year. One important lesion from this review was that many different NETs can contribute to the required 10 to 20 Gt of CO₂ that need to be removed from the atmosphere each year. <u>No one NET needs to do it all or would be expected to do it all</u>. We recommend that in the U.S. government and other governments of the world, support a wide range of NETs with especially attention to supporting EW and the **3 OAEs**.

In Conclusion:

- by eliciting the cooperation of all countries to MINE, GRIND, SPREAD climate rocks to SEQUESTER the amount of CO₂ they emit,
- by emphasizing the economic advantages,
- by using zero carbon dedicated sources of energy for grinding,
- by using commercial waste sources of silicates (tailings),
- by factoring in the increases in crop yield,
- by factoring in the decrease in pH of the soil,
- by combating CO₂ emissions from soils and oceans,
- by combating N₂O emissions from the soil and ocean,
- by increasing ocean alkalinization,
- by combating ocean acidification,
- by combating ocean warming,
- by combating ocean deoxygenation,
- by emphasizing the use of EW at weathering "hot spots",
- by setting up artificial weathering hot spots anywhere,
- by focusing on areas of oxisols and ultisols,
- by using carbon negative ships for eOAE and heOAE,
- by determining the amount of Ni and Cr in the rocks before using them,
- by the judicious planting of Ni hyper-accumulator plants,
- by partnering with New Caledonia to open their vast reserves of ultramafic rock to serve the south Pacific area,
- by using *in situ* approaches in New Caledonia and other areas suitable for *in situ* sequestration,
- by urging the U.S. Military to start a project analogous to the Manhattan Project, to mine, process and stockpile ultramafic rocks at the Twin Peaks site in WA and other sites in the US and throughout the world.
- by partnering with other government agencies such as the Department of Agriculture, U.S. Geological Service, Department of the Interior, NOAA, NOAA OAP, EPA, the Biden Climate Group, and others,
- by setting up a US Department of EW/OAE,
- by urging the UN to set up a Global EW Organization (GEWO),
- by using funds set aside for global mitigation for EW/OAE,
- by also considering heOAE that does not use ultramafic rocks,
- by urging the U.S. Navy to use heOAE technology on its nuclear powered ships,
- by urging the U.S. and other governments to the support the use of EW, OAE, eOAE and heOAE to remove atmospheric CO₂,
- by directing the DOE and Nuclear Regulatory Commission to fast track the approval of super safe molten salt nuclear power plants for providing carbon free electrical power for grinding climate rocks and providing the electricity for heOAE.
- **EW, OAE, eOAE and heOAE could become the major NETs to safely remove gigatons of CO2 from the atmosphere.**

So, What Do We Recommend?

- **1. Do the above.**
- 2. Develop Blueprints for zero carbon eOAE ships USING OLIVINE and support their construction and use, and/or advocate for the Navy and NOAA to carry this out.
- 3. Develop Blueprints for zero carbon heOAE ships NOT USING OLIVINE (heOAE) and support their construction and use, and/or advocate for the Navy and NOAA to carry this out.
- 4. Advocate for the Navy to develop a fleet of nuclear powered heOAE ships.
- 5. Advocate for the Government, US Army, and Engineering Corps to Develop a Large-Scale Mining and Production Site at Twin Peaks, WA, and other sites.
- 6 Advocate for the Global Cooperation for EW by mining, processing, and using ultramafics to sequester CO₂.
- 7. Carry out the recommendations listed in the Addendum: How the Different Parts of the U.S. Government and the Private Sector Can Help with Using Enhanced Weathering, OAE and eOAE to Combat Global Warming

2. Develop Blueprints for zero carbon OAE ships USING OLIVINE and support their construction and use, and/or advocate for the Navy and NOAA to carry this out.

To ensure they do not produce more CO_2 than they sequester eOAE and heOAE ships need to be designed to run on carbon free electricity for both power and the electrochemistry. The ships would need to comply with the International Maritime Organization Energy Efficiency Design Index (EEDI) standards, but preferably do far better.

Power can come from **solar panels**, wind turbines, sails, fuel cells and mid-ocean solar/wind turbine islands, OTEC (ocean thermal energy conversion), and nuclear power. Research is needed to determine what is the best mix of these?

Batteries Some form of battery storage will be necessary for those days when the sun is not shining, or the wind is not blowing or both. Currently there are two possibilities – lithium and iron-air batteries. A problem with lithium batteries is that they are sensitive to high temperatures and inherently flammable. These battery packs tend to degrade much faster than they normally would, in the presence of excess heat. If a lithium-ion battery pack fails, it can burst into flames and can cause widespread damage. This would be a disaster for a ship that might spend a lot of time at the equator. Solid state Li batteries would be preferable.

Iron-Air battery Form Energy's New Low-Cost, Iron-Air Battery. https://singularityhub.com/2021/08/02/form-energys-new-low-cost-iron-based-battery-runs-for-100-hours/ **Form Energy's** batteries are each about the size of a washing machine and are filled with iron pellets and a water-based electrolyte like that used in AA batteries. To discharge, the battery breathes in oxygen from the air, converting the pellets to iron oxide, or rust, and producing electricity in the process. To charge, the application of a current converts the rust back into iron and expels the oxygen. The key to their approach is the low cost of the constituent materials. Today's lithium-ion batteries cost \$50 to \$80 per kilowatt-hour thanks to the expensive minerals required to make them, like nickel, cobalt, lithium, and manganese. According to the Wall Street Journal, Form Energy can make their battery for just \$20 per kilowatt-hour, and they will be able to provide power for 100 to 150 hours, depending on the configuration. We anticipate the Form Battery will be available in time for the eOAE and heOAE ships.

Solid-state Electrolyte Lithium Batteries. These are another much more powerful and efficient type of battery that will soon be available. They should be less susceptible to burning. A Chinese company, CATL, recently announced the development of a semi-solid state lithium battery with twice the energy density of standard lithium batteries.

NASA's Nickel-hydrogen batteries might be ideal. See addendum.

Engineering questions for both OAE and eOAE using olivine, it will be necessary to determine what amounts of CO₂ sequestration could each boat accomplish? If olivine is used, how many tons of rocks could the boat carry? What would be the optimal balance between size, efficiency, carbon-free electricity and motors, and cost? What are the best electrolytic methods for eOAE? Should the ships carry the capability for more than one method of electrolysis?

Effects on Ocean Chemistry? What are the effects these alkalinization projects on the ocean chemistry? This can be answered using mesocosms.

On-board chemistry laboratory Such a laboratory will be necessary to determine pH, salinity, alkalinity, temperature, pCO_2 , pO_2 , as well as all the members of the carbonate cycle Ω carbonate, CO_2 , H_2CO_3 , HCO_3^- and CO_3^{2-} for mesocosm and ocean sampling. Should samples simply be collected for analysis on land or should be the ship equipped with sophisticated instruments such a mass spectrometer? What other instruments are needed? The use of Wave Gliders (Chavez, 2018) to measure surface pH and pCO₂ at significant distances from the ship would be a valuable addition to the instrumentation. There will be a need to assay heavy metals such as nickel, cadmium, and others. Is best done by mass spectroscopy?

Loading For OAE and eOAE ships, how will the loading and storage of ultramafic rocks be carried out? Can the boat be designed to self-load? Is there a need for onboard loading towers?

Governance What governance agreements will be necessary. The initial use of the OAE/eOAE ship would need to basically be a research laboratory to satisfy various governance rules. If this shows that if the benefits far outweigh any negatives, this will pave the way for large scale OAE/eOAE. What departments in the US government handles that? NOAA? NOAA-OAP? The UN?

Crew and Crew Cabins Obviously there is a need for cabins for the crew. But what is the makeup of the crew? Most likely: the captain, first officer, mechanics, engineers, electricians, chemists, marine biologists, cooks, and others. But to save funds for heOAE ships, volunteers could perform most of the duties.

Number of Ships Needed. Harvey (2008) spoke of a fleet of thousands of ships, and time spans of up to 100 years. Hopefully, mechanisms can be found to drastically reduce this number and time span. He also provided detailed analysis of three different sized ships, with capacities of 2,500, 25,000 and 250,000 tons. Large oil tankers have a capacity of 600,000 tons. To ensure efficiency it is likely the OAE, eOAE research ships should have a capacity of at least 250,000 tons.

If the results with the initial research ship are positive, multiple countries and many ships could then be involved. The goal is to provide a standardized set of blueprints for proven ships, so each country does not have to design and research its own. There may be only one or two ship building companies building the ships and different countries would purchase their ships from these companies.

There is a possibility that heOAE technology and its deployment could significantly reduce the above figures.

3. Develop Blueprints for zero carbon ships Not Using Olivine (heOAE) and support their construction and use, and/or advocate for the Navy and NOAA to carry this out.

While EW and OAE utilizing finely ground ultramafic rocks has many advantages over DACS, there are a few negative issues, including the ecological effects of mining, the cost of mining and grinding, and the cost of transporting and spreading the rocks on land or ship based OAE. Some procedures directly extract CO_2 from seawater and indirectly from the atmosphere without using alkaline rocks. We call this heOAE.

In addition to avoiding the need to mine, grind and distribute ultramafic rocks, there are the following additional positive aspects of shipboard heOAE.

1) It would avoid the NIMBY and governance issues as well as the costs of land-based operations.

2) It would avoid any concern about whether the massive deposition of ultramafic rock products in the ocean might pose problems with heavy metal contamination, since it does not use olivine but simply uses electricity to rearrange the pre-existing chemistry of the ocean.

3) Being ship based it could concentrate on specific areas of the ocean such as those involved in outgassing of large amounts of CO_2 and areas where corals are dying.

4) Being ship based it could concentrate on specific areas of the ocean where variations in seawater temperature result in different concentrations of CO_2 . The higher the CO_2 concentration the more effective the heOAE would be. These areas may preferentially be in the Southern Ocean.

A **catamaran** type ship might be useful since they are so stable. It could have sails to provide carbon negative power for locomotion, and a large surface area for solar panels and wing turbines to provide power for the electrolysis unit. Fuel cells running on hydrogen would also be used. As noted above they could re-coup 50% of the electrical energy needed for electrolysis. With high-capacity Ni-hydrogen batteries the ship could periodically renew the batteries at open ocean solar farms (see pages 211-212). The full development of this approach will require research involving a team of marine architects, electrical engineers, and electrolysis experts.

If this approach proves to be feasible, it could provide a model for many countries, NGOs, non-profits, or activist individuals, to purchase and sail such ships. This result in a fleet of many hundreds of such ships traversing the oceans of the world sequestering CO_2 at minimal cost.

Nuclear Powered eOAE Ships

4. Advocate for the Navy to develop a fleet of nuclear powered heOAE ships.

An alternative to using solar islands and wind turbines to power eOAE ships is the use of nuclear-powered ships. The U.S. Navy has 10 nuclear-powered aircraft and 72 nuclear powered submarines. They make up about forty percent of major U.S. naval combatants, and visit over 150 ports in over 50 countries, including approximately 70 ports in the U.S. and three in Japan. Clearly the U.S. Navy has the expertise to develop nuclear powered eOAE ships.

The war on global warming could be more important than any conflict since WWII.

A world-wide combined use of EW, CaO, MgO or Mg(OH)₂ based OAE, eOAE using olivine, and heOAE without ultramafic rocks, plus some of the other lesser NETs,

could bring the total of sequestered CO₂ to 10 - 20 Gt/yr without requiring the potentially dangerous burial of gigatons of CO₂.

5. Advocate for the Government to Develop a Large-Scale Mining and Production Site at Twin Peaks, WA, and other sites.

We recommend that the U.S. Military/Army Engineering Corp (or other U.S. government organization) develop a centralized facility of olivine mining, grinding, and distribution at the Twin Sisters site in WA and other places in the U.S. A critical aspect would be the closeness to a major port at Bellingham and the availability of renewable energy. This could come from the hydroelectric power in Southern Washington, or from the utilization of a Molten Salt Nuclear Reactor or other Microreactor on site, or a wind or solar farm. Other sites in Oregon and California are also close to the ocean facilitating use for eOAE and distribution by boat of ground olivine.

Lynden Maple Falls Glacier erndale 539 Deming 5 42 Deming Bellingham 1 5 9 Map data ©2021 Google

As shown below, it is only 22 miles from the Twin Sisters site to the Bellingham port.

An advantage of utilizing the U.S. Military is that they would be able to accelerate the use solar farms, wind farms, or Molten Salt Reactors or Microreactors as a source of energy for grinding the ultramafic rocks. Given the speed with which the military initiated and completed the Manhattan Project the launching of a new Manhattan type Project for activating EW, OAE and eOAE may be necessary.

In the U.S. the **Army Corp of Engineering** which already has a **Climate Preparedness and Resilience Program** could be given the job of mining and developing such stockpiles of ground olivine. Given their ability to complete large projects, this would be the ideal agency to develop these facilities.

The best approach might be to work closely with **Olivine Corp** since they are already mining at this site. The government could fund them to dramatically increase the amount of ultramafic rocks they mine and ensure they are used for EW and OAE, or simply buy the company.

6. Advocate for the Cooperation of All Countries to Mine, Grind and Spread Climate Rocks to sequester the CO₂ they emit.

This type of world-wide cooperation is not unique. For example, in 2006 when it was realized that fusion works better the larger the tokamak, a group of 35 countries meet at Elysée Palace and signed an agreement to build the ITER. Significant advances are currently being made in fusion energy with 36 different companies using many different innovative approaches with much more powerful magnets and smaller tokamaks.

Another example of the speed with which many countries can come together for a common goal is the **Sustainable Development Goals (SDGs) project.** In September 2015, **193 countries came together at the United Nations** to adopt and commit to a long-term, comprehensive strategy to tackle the world's greatest challenges related to global sustainable development. The result was the SDGs, a list of 17 goals to achieve a better and more sustainable future for all by 2030. More recently, 193 countries came together to attempt to solve the problem of plastics in the ocean (Stokstad, 2022).

We need a comparable group of countries to come together for a EW/OAE/eOAE/heOAE conference devoted to an international effort for all countries.

So, what is the magnitude of the problem? How much is 10 gigatons of Rock?

Since visuals are better than text, we will give that a try. In the NOVA production *Polar Extremes,* Kirk Johnson showed an artist's picture of what **12.5 gigatons of charcoal would look like**. This represents only part of the amount of carbon humans put into the atmosphere each year. **The pile was over a mile high and 4 miles wide.**



A 12.5 gigatons of rock

If it takes at least 1 ton of ultramafic rock to sequester 1 ton of CO₂, it will require a pile almost 2 or more times as large as this to remove 20 gigatons of CO₂. Since other NETs will probably be contributing to the removal of CO₂ this is a top estimate. Nevertheless: it is **impossible to extract and sequester huge amounts of CO₂ from the atmosphere using EW**, **OAE and eOAE**, without mining an equally large amount of processed ultramafic rocks. This will clearly require an international effort.

There are many sites, in many countries with deposits of ultramafic rocks. However, there are three major problems.

1. It is estimated that approximately 10 - 20 gigatons of olivine will be needed for the EW and OAE NETs. Norway produces 2 mt/yr and this represents half of the world's supply. The olivine currently mined is a tiny reaction of what is needed.

2. Virtually all the current world's supply of mined olivine and related ultramafics is being used for purposes other than CO₂ sequestration, such as in steel smelters and foundries and brick, tile, concrete, aggregate and abrasives manufacturing. Virtually none of it is currently used for sequestration of CO₂.

3. Most of the deposits described are known because of geologic studies reported in geologic journals and only represent potential sources, i.e., the most of the ultramafics we need are all still in the ground.

In conclusion, there is currently zero supply of mined olivine and other ultramafics specifically for use for EW/OAE/eOAE NETs. We are essentially starting at ground zero.

Ultramafics in the US

The United States contributes 25 percent of the total greenhouse gases to the atmosphere. The optimal approach to beginning to initiate the EW and OAE NETs will be to determine if enough dunite is available in the US to get operations started. The following table from Taylor et al (2016) Supplemental indicates there are significant deposits in the US and Canada alone.

Estimated Global Dunite Reserves Taylor et al, (2016) Supplementary Information

Only the largest sites are included:

Country	Location	Potential Reserves Pg*
Australia	Owendale complex	3.7
	Tout complex	11.6
	Avondale	1.5
Canada	British Columbia	45.0
China	Songshugou massif	33.2
	Unmeasured ultramafics	66.0
	Ophiolites	11.5
Greenland	Greenland	8.2
Japan	Horoman Hill	10.5
New Zealand	Almklovdalen	7.8
Russia	Galeomean complex	17.2
	Kondyor massif	33.5
Sweden	Arutats	1.8

USA	Twin Sisters	256
	Alaska	43.9
	North Carolina & Georgia	1.6
Turkey	Ophiolites	48.0
Oman	Ophiolites	1,650
Totals	USA & Canada	346.5
	Total – Oman	601.0
	Total + Oman	2251

* Pg (Pentagrams)

One of the best sources about deposits in the US has been provided by Golf and Lackner (1998) in the section of their paper called **Best Ultramafic Ores for Carbonate Disposal.** The following summarizes these sites.

1. Twin Sisters Dunite This is the largest body of dunite in the United States (Ragan, 1963), It occurs in the Cascade Range of northwestern Washington. This dunite body covers about **90 km²** and is presently mined by **open-pit methods** for refractory (foundry) sand. An examination of a 20-kg sample provided by the operator showed that it contains only about 4% serpentine and other secondary reaction products.

2. Green Mountain Peridotite The relatively large, un-serpentinized Green Mountain Peridotite (about 5 km²) occurs in the Appalachians of **North Carolina** and is also mined primarily for foundry sand. An examination of this material showed that it contains about 5% orthopyroxene and about 10% of high-grade metamorphic products including talc and Mg-rich amphibole. This material is less desirable than is dunite as a CO²-sequestering ore even though it contains nearly comparable amounts of Mg (Goff et al., 1997).

3. Belvidere Mountain prospect in Vermont (Labotka and Albee, 1979).

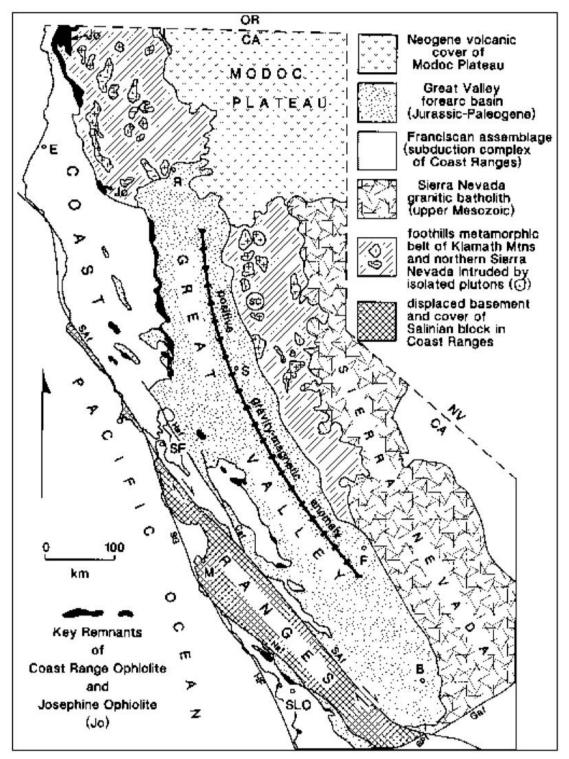
4. Canyon Mountain and Vulcan Peak deposits in **Oregon** (Himmelberg and Loney, 1973; Thayer, 1977).

5. Del Puerto and Burro Mountain. **California** This is part of an elongate slab of ophiolite whose ultramafic part (up to 300 m thick and about 40 km²) is variably serpentinized (Evarts and Schiffman, 1982); Himmelberg and Coleman, 1968; Goff et al., 1997).

6. Stillwater Complex

7. Wilbur Springs Serpentinite. The serpentinite is the preserved base of an extensive, north-trending sheet of ophiolite that is about 50 km long and averages 2 to 6 km wide. The thickness of the deposit varies from a few tens of meters on the west to several hundred meters on the east (McLaughlin et al., 1989). Most of the land occupied by the serpentinite belongs to the U.S. Bureau of Land Management or to a few cattle ranches.

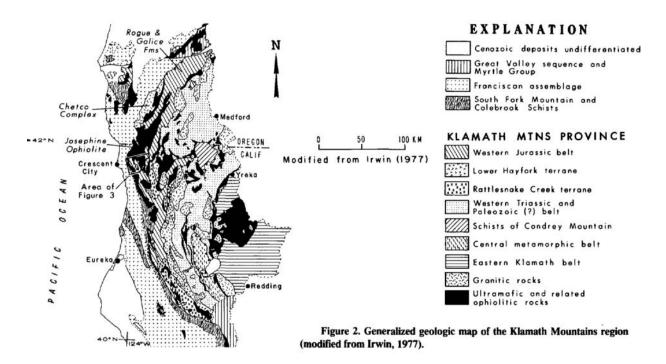
8. CA Coast Range Ophiolites and Josephine Ophiolite Perhaps the largest body of continuous serpentinite outcrop in the United States occurs at the Josephine Ophiolite of northwest California and Oregon, which extends over about 800 km² (Harper, 1984). These deposits, although some are huge, are mostly serpentinized harzburgite and are not as desirable as the unaltered dunites.



Geologic sketch map of part of California showing the regional relation of the Coast Range Ophiolite to key lithotectonic belts; SC—location of Smartville ophiolitic complex within foothills metamorphic belt; trend of Great Valley gravitymagnetic anomaly (high) after Cady (1975).

Note the presence of key remnants of the Coast Range Ophiolite stretching from Oregon border along the western edge of the Great Valley to central California. Additional details about

the **Josephine Ophiolite Complex** at the Oregon-California border are shown in the following map.



The minerals in this complex consist of harzburgite, gabbro, dunite and other ultramalfics (Harper, 1984)

The Belvidere, Vulcan Peak, Del Puerto, and Stillwater bodies contain small zones (4 km²) of relatively **unaltered dunite**.

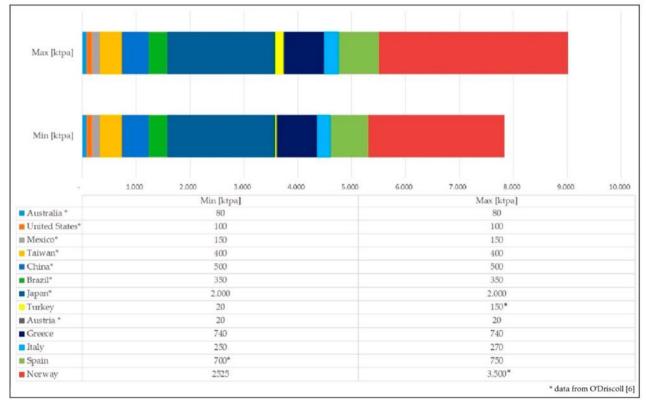
Completely serpentinized peridotite is exceptionally common in certain areas of eastern and western North America. Ultramafic rocks in the Baltimore Complex contain about 80% serpentinite and **most of the California deposits consist of mostly sepentinite**.

An important question is - are serpentines suitable for *in situ* storage? If they are this would provide an excellent use of California serpentines, since they are less suitable than olivine for EW.

Goff & Lackner (1998) stated that small ultramafic bodies of about 1 km³, can potentially sequester about 1 gigaton of CO₂. "A single large deposit of dunite (about 30 km³) could dispose of nearly 20 years of current (1998) U.S. CO₂ emissions." Given that most of the sites reviewed above are of that size or larger, given sufficient effort we should be able to develop a very large stockpile of ultramafic rock both native and serpentized, in the US alone. That is an effort that needs to be started.

Ultramafics Worldwide

The following figure shows the **current world's production** of periodite (minerals rich in olivine).



World production of periodite (Current numbers for the production from the producers of the investigated samples. Data from O'Driscoll, 2004). Figure from Kremer et al (2019).

The total world supply of periodite is between 4,200 and 5,400 kilotons/yr or **4.2 to 5.4 gigatons/yr**. However, if the goal is to sequester 20 gigatons of CO_2/yr and it requires at least 1.5 tons of ultramafic rock to sequester one ton of CO_2 , and olivine constitutes about 80% of periodities, that means a total of up to 38 gigatons of periodite per year will need to be mined. In addition, as stated, the vast majority of the current supply of olivine is already spoken for and used for other things. To obtain a huge supply of olivine and ultramafic rocks for CO_2 sequestration and EW we virtually must start from scratch. Some countries such as New Caledonia, New Guinea and others have large undeveloped supplies of periodite.

See Appendix C. Worldwide Ultramafic Mining Sites and Companies for a detailed presentation of world-wide deposits of ultramafic rocks.

Funding the Mining start-ups in other countries. We believe that the **Green Climate Fund**, with its billions of dollars, could supply the necessary funding to countries around the world to begin these mining, processing, and using operations.

In conclusion, EW, OAE and eOAE cannot work without the international development of huge stockpiles of processed ultramafic rock. As was so readily done with the ITER and SDGs, we would strongly urge a similar meeting of all countries with deposits of ultramafic rocks to begin mining operations to produce, process, stockpile and use these rocks solely for the purpose of EW and OAE. Money in the Green Climate Funds could be used to jump start these projects.

How Can the U.S. Federal Government Help?

(This is developed in more detail in the **addendum**)

There are many Federal agencies that should have a programmatic interest in combating global warming and would be of great help in supporting the various efforts in the area. The following are some of the agencies that can be of help. Most research on CO₂ subsurface *in situ* injection and carbon mineralization at the laboratory have been financed by the DOE and the National Science Foundation (NSF), with support from the Environment Protection Agency (EPA), the US Geological Survey (USGS) and the Bureau of Land Management (BLM).

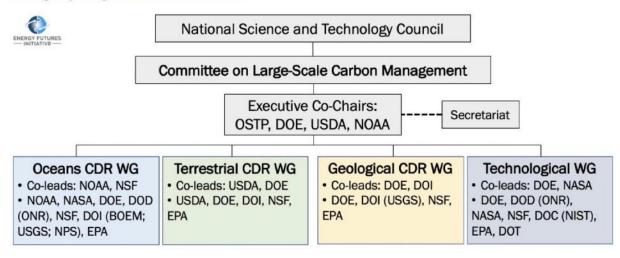
The magnitude of CDR is so immense that the authors of EFI (2019) proposed the involvement of following multiple federal entities. Further details concerning the involvement of the US Government are given in the attached Addendum: How the Different Parts of the U.S. Government and the Private Sector Can Help with Using Enhanced Weathering and OAE to Combat Global Warming



Federal Participation in CDR RD&D Initiative

EFI (2019) proposed the formation of a new entity the **Committee on Large-scale Carbon Management** utilizing these federal entities in the following manner.

Interagency Integration and Coordination



The Military - DOD

In his book, *All Hell Breaking Loose. The Pentagon's Perspective on Climate Change*, Michael Klare documents in detail the **US Military's deep concern about how climate change is impacting the security of the United States.**

"Top military officials perceive climate change as a secondary but insidious threat, capable of aggravating foreign conflicts, provoking regional instability, endangering American communities, and impairing the military's own response capabilities. Worse yet, warming's impacts are expected to grow increasingly severe, complicating the Pentagon's ability to address what it views as its more critical tasks."

The risks to the military were felt to occur on two fronts.

1. The risk to military installations world-wide.

2. The risk that droughts, desertification, excessive heat, rising seas, hurricanes, floods, and forest fires will cause instability of some nations resulting in mass migrations, disputes, and wars.

Regarding the first, Congress directed the Department of Defense to conduct a full-scale assessment of climate-related threats to all US military bases – a total of 3,500 installations. An interim report *Climate-Related Risk to DOD Infrastructure: Initial Vulnerability Assessment Survey* was released January 2018. The greatest reported impact was from drought with 782 facilities (22% of all bases) experiencing some drought conditions, 763 bases reported impacts from strong winds, 706 from severe flooding, and 210 from wildfires. It was stated that these bases are launch platforms and "You can't fight s war unless you have a place to leave from."

As if to emphasize the danger, a few months after the report was released Hurricane Micheal inflicted catastrophic damage on Tyndall Air Force Base in the Florida Panhandle, home of the super-sophisticated F-22 Raptor fighter planes, each costing \$339 million. Senior military officials agree that climate change is not some far-off future problem, it is happening now.

Regarding the second, "Pentagon analysists highlight the deleterious effect of climate change on vulnerable populations, fragile states, and brittle institutions around the world. They

see climate change as **ratcheting up global chaos**, which in turn means greater likelihood of U.S. involvement in ugly foreign wars."

Rear Admiral David Titley, former chief oceanographer of the U.S. Navy, noted that this, "can exacerbate or inflame tensions within or between states. **These problems can lead to state** failure, uncontrolled migration, ungoverned spaces...and terrorist activity."

Climate change will produce an increased call on U.S. Forces to provide humanitarian aid and security services known as "stability operations."

The collapse of economic and governmental institutions in numerous areas of the globe would disrupt vital trading networks and **help foster deadly pandemics**. In worst case scenarios, the major powers will fight over water and other vital resources, producing new global rifts and potentially involving the United States in full-scale ward with nuclear armed belligerents.

The American military will lose its capacity to defend the nation from multiple foreign perils, while the homeland itself will be ravaged by storms, floods, droughts, fires, and epidemics. And this was only the first few pages of the book!

In the most recent report by the DOD (2021) includes the following statement, "**There is** little about what the Department does to defend the American people that is not affected by climate change."

Klare stated, "As we write this, in September 2021, all of the above is already happening."

U.S. Stockpiles of Ultramafic Rocks

So, how does all this relate to our immediate goals? The situation with EW/OAE is similar to the problem with hydrogen powered cars. No company will make such cars when there are no hydrogen fueling stations in place around the country. And no one is willing to front the expense of setting up hydrogen fueling stations if there are no cars to use them. As pointed out above, there are currently virtually no mining companies that mine ultramafic rocks just for their use in EW/OAE projects, because currently, there are essentially very few of these projects.

Given the U.S. government's agreement that climate change is a critical issue for our national security, and given the **reality that prevention is cheaper and better than endless mitigation**, they have a pressing reason utilize the help of the many government agencies that could be involved. In the following sections propose some critical programs and suggest which different government agencies might be involved.

The U.S. Navy and OAE/eOAE/heOAE Ships

Michael Klare pointed out in his book, that the U.S. Navy has an interest, short of atomic powered vessels, of decreasing the use of fossil fuels for it fleets. Thus, they may be interested in lending their expertise to our goal of developing a OAE, eOAE and heOAE ships running entirely on renewable but non-nuclear energy sources.

Perhaps, given the concern of the Military about the world-wide destabilizing effects of climate change, the Navy would find it would be very much in their interests to build a fleet of OAE/eOAE/heOAE ships and **initiate a program to train the specialized crews needed to man them**. Since the U.S. has the largest Navy in the world, this would go a long way toward combating global warming and the destructive effects of ocean acidification.

The U.S. Navy is also uniquely positioned to develop nuclear powered heOAE ships by retrofitting its 10 nuclear powered aircraft carriers and 72 nuclear powered submarines with eOAE technology. They could also devote Nimitz class aircraft carriers destined to be

decommissioned, entirely to heOAE technology. This could sequester a gigaton or more of CO_2 /year, 1,000 to 2,000 times that of a single DACS unit. In addition, as stated above, the ongoing yearly costs for the rest of the century would be many billions of dollars less than those for DACS, EW and olivine based OAE.

NOAA, NOAA OAP (Ocean Acidification Project)

The National Oceanic and Atmosphere Administration and NOAA OAP has an interest in many different aspects of climate change and many of these could be of help in our projects. Some of the specific areas they might be of help are as follows.

• Help with the design and building of the OAE/eOAE/heOAE carbon free ships.

• Help with the design of solar or wind turbine islands to power heOAE.

• Help with the governance and international laws potentially involved in spreading finely ground ultramafic rocks in the ocean.

• Help with the question of whether focusing alkalinization efforts to areas of CO₂ outgassing is reasonable.

• Help with the question of whether focusing on the area of the great barrier reef would be worthwhile.

• Interact with the Navy to build carbon free OAE/eOAE/heOAE ships and develop a new Navy OAE/eOAE/heOAE Corps to educate and train sailors to man and use these ships.

• Provide OAE ships and training internationally.

The following may be a helpful contact.

The Geophysical Fluid Dynamics Lab (GFDL) When the Intergovernmental Panel on Climate Change (IPCC) released its Sixth Assessment Report, **Vaishali Naik** and many of her colleagues at the GFDL contributed to the scientific results. As a physical scientist at GFDL, she is a part of the biogeochemistry, atmospheric chemistry, and climate division for the NOAA laboratory in Princeton, New Jersey. She is a coordinating lead author of the chapter on "Short-lived Climate Forcers," contained within the Working Group I Sixth Assessment Report.

National Ocean Service should also be interested in this project.

EPA

If there was ever an important issue related to environmental protection it is global warming, which has the capacity to devastate our environment. The EPA will also be involved in granting permissions to carry out OAE/eOAE measures in US areas and with US ships (NAS 2021).

Nuclear Regulatory Commission (NRC) and Oak Ridge National Laboratory

The U.S. Nuclear Regulatory Commission (NRC) was created as an independent agency by Congress in 1974 to ensure the safe use of radioactive materials for beneficial civilian purposes while protecting people and the environment. The NRC regulates commercial nuclear power plants and other uses of nuclear materials, such as in nuclear medicine, through licensing, inspection, and enforcement of its requirements.

Because of some scary nuclear reactor accidents, such a Chernobyl, Three-mile Island and Fukushima-Daiichi, many people are justifiably afraid of nuclear power. This was such a problem for some governments that most of the nuclear power plants in Germany were shut down and the building of new reactors in the U.S., has largely come to a stand-still. In the 1960s **Dr. Arvin Weinberg**, then Director of the Oak Ridge Laboratory, had an operating **MSR** (**Molten Salt Reactor**) **successfully running for two years**. Ironically, President Nixon shut down this program because it did not produce the plutonium needed for bombs. A **Molten Salt Reactor is super safe and cannot suffer a melt down since it is in a constant melt down state**, which is an inherent part of its operation. If an earthquake or tsunami occurs, if all the operators die, if all the electricity stops, and other ifs, a freeze plug melts and the molten salt drains to underground holding tanks and the reactor stops. In addition, nuclear waste is a fraction of that of Light Water Reactors (LWRs) and in fact can use as fuel the waste from LWRs. For details on Dr. Weinberg and the MSR technology see www.thecomingsfoundation.org Go to Molten Salt Reactors.

It could be argued that if MSRs rather than LWRs were used to produce electrical power, their inherent safety, lower cost, and modularity would have resulted in the rapid replacement of coal powered electricity and the rapid accumulation of global warming CO₂ would never have happened. It is not too late to resurrect this important technology.

If one were to fantasize about an ideal solution to replacing fossil fuels with renewable energy some of the requirements would be:

- zero carbon footprint,
- able to burn up waste from LWRs,
- cheaper than coal,
- inexhaustible energy supply,
- minimal waste,
- capable of producing both electricity and fuel,
- relatively inexpensive,
- no environmental impact (no threat to birds as with wind turbines or the desert as with solar).
- modular (thus avoiding the gigantic gigawatt reactors).
- does not require long power lines as with wind and solar.
- very safe.
- resistant to earthquakes (i.e., Fukashima)
- resistant to meltdowns (i.e., Chernobyl, Three Mile Island)
- resistant to terrorism
- affordable to developing nations.

MSRs satisfy all these requirements. Ironically, several years ago China downloaded all the available information on MSR publicly available at the Oak Ridge National Lab and **committed five billion dollars to the effort**. They recently announced the development of working MSRs. Thus, **they are taking our technology and doing what we should have done decades ago.**

There are several companies that are developing Molten Salt Reactors. We believe that **Terrestrial Energy** is the furthest along. There are two parts of this company – **Terrestrial Energy Canada** and **Terrestrial Energy USA.** In personal communications the Canadian branch expects to be approved in 2025 and the U.S. branch in 2030.

The US Government needs to do all it can to support and facilitate the development and approval of Molten Salt Reactors and the associated companies. They can solve all the needs for the energy of grinding and heating, to facilitate the dissolution of ultramafic rocks on cropland and the ocean. They could also provide the energy for releasing captured CO_2 in DACS and heOAE, to say nothing about their ability to provide carbon free electricity.

This exciting technology can play a major role in replacing coal, oil and gas fired power plants with carbon zero plants.

FEMA

According to its director, Dianna Chriswell, The Federal Emergency Management Administration has placed fighting global warming as a goal. When funds become available a question for them is how to help. We suggest that assisting in the projects outlined in this document would be a good place to start. They stockpile many items as part of their emergency management. We suggest that stockpiling ultramafic rocks to have them available for use on croplands and the ocean, would be an important part of their efforts.

DOE Department of Energy

If nuclear power was used to grind ultramafic rocks at the Twin Sisters site, the DOE would play a major role. See also above under the DACS, the proposals from Fossil Energy and Carbon Management at the Department of Energy.

Recently, DOE Secretary Granholm launched Carbon Negative Earthshots program to Remove Gigatons of Carbon Pollution from the Air by 2050 and keep the price below \$100 per ton of CO₂ sequestered. This is an excellent beginning. However, the potential problems with DACS are listed above (p 21-24). We believe EW, OAE, eOAE and heOAE is needed as either a much better approach or supplement to DACS.

CIA

The CIA assessed that the effects of a changing climate and environmental degradation will create a mix of direct and indirect threats, including risks to the economy, heightened political volatility, human displacement, and new venues for geopolitical competition that will play out during the next decade and beyond. The degradation and depletion of soil, water, and biodiversity resources almost certainly will threaten infrastructure, health, water, food, and security, especially in many developing countries that lack the capacity to adapt quickly to change and increase the potential for conflict over competition for scarce natural resources.

Clearly the CIA should have an interest in these projects.

US Department of Agriculture

The use of EW on cropland should be of critical interest to the USDA. They could play a major role in farmer education in the use of this NET.

U.S. Department of Commerce

The Department of Commerce could take the lead in helping other countries to develop a new industry around the mining and use of Climate Rocks and in distributing ground climate rocks to NGOs and non-profits for individual use and for the drone program.

Department of the Interior

Since some of the ultramafic deposits are on federal land the Department of Interior can play an important role on these projects. In addition, if the vertical hot weathering site concept works the Department of Interior and U.S. Geological Survey would play an important role in identifying appropriate sites.

U.S. Geological Survey

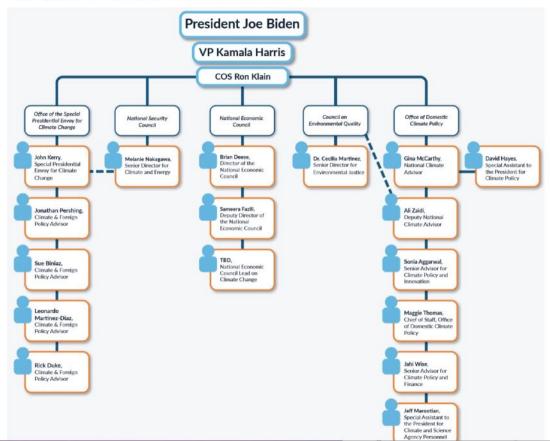
The USGS would play a very important role in identifying the best sites for mining Climate Rocks in the U.S. and in cooperation with similar departments across the globe develop a comprehensive data base world-wide for such sites. The database would include the location of suitable tailings.

Department of State

Obtaining the cooperation of all the countries of the world will undoubtably require some diplomacy. The Department of State would play a major role in this. They could especially play an important role in cooperating with New Caledonia to develop their large deposits of ultramafic rocks.

The Biden Climate Team

Of all the above federal agencies the Biden Climate Team may be the most important. To pursue this area of research we would need a special team working with the U.S. Office of the Special Presidential Envoy for Climate Change was headed by John Kerry who has moved on to assist in Biden's re-election campaign. John Podesta is currently the envoy for climate change. As shown in the following diagram, within this team there is considerable emphasis on Foreign Policy.



Key Figures in President Biden's Climate Team

We would ask the Biden Group to help with the following proposals.

1. Provide assistance with the development of an OAE/eOAE/heOAE ships and interaction with the Navy and NOAA-OAP to build and man the needed ships.

2. Encourage the Navy to retrofit its 10 nuclear powered aircraft carriers and 71 nuclear powered submarines with heOAE technology, if and when it is available.

3. Initiate the Twin Sisters Project.

4. Develop Global Cooperation for Mining Ultramafics

Here we would also ask the Biden Climate Team for assistance in the following.

- Initiate an International Enhanced Weathering Consortium.
- Put together in each country an NET EW/OAE team of experts, including in the US.
- Identify the location of mineable mafic and ultramafic rock deposits in their country. As shown above, there are many possibilities other than olivine. I have been impressed that every time I examine in detail the location of ultramafic rocks in different countries, they are almost always close to the coast: Norway, United States, Columbia, Australia, New Guinea, and New Caledonia. This is undoubtedly due to the mechanism of how they are produced, i.e., by the movement of tectonic plates. This costal location is ideal for spreading such rocks in the ocean as well as supplying other countries.
- Initiate the mining of those rocks.
- Develop a source of clean energy for the crushing and grinding of the rocks.
- Develop suitable methods of storing and transporting the ground rocks.
- Identify suitable ports and techniques for placing the ground rocks on ships.
- Identify for that country the most suitable use of this product on cropland, noncropland, in rivers, in the ocean, or simply supplying other countries.
- Those countries that have access to the ocean may prefer to put their ground rocks into the ocean. If so, the development of standardized plans for a ship using renewable energy to distribute rocks for alkalinization, would be very beneficial. Determine if the country is willing to purchase one or more of these ships.
- Determine the amount of credit they each country can receive for these efforts.
- Develop techniques for monitoring the efficiency and long-term effectiveness of CO₂ sequestration by EW and the 3 OAEs, and risk assessments including assessing trace metals.

• We would envision that each country put together a team consisting of geologists to identify the best deposits of ultramafic rocks, mining engineers to determine the best approach to the mining, environmentalists to help minimize environmental impact, electrical engineers to set up the solar panels, mechanical engineers to determine the best methods of grinding, farmers to monitor to use of the rocks on farmland, economists to determine the amount of CO_2 emitted based on amount of gasoline, oil, natural gas and coal consumed, PR people to develop public support and politician's to ensure the smooth operation of the whole undertaking. If any of these specialists are not available, a UN Global EW Organization could supply them.

Working with New Caledonia. This nation could become a major supplier of ultramafic rocks in the Pacific Area including for combating equatorial CO_2 outgassing. It is also a potential site for massive storage of CO_2 by *in situ* hybridization. How do we get that started? It is a French Colony. Do we approach the President of France or the local government, or do we start with one of the authors who have published studies this area, such as Pierre Gautier? This is essentially a task for the U.S. government and the Biden team.

5. Set up a Department for Enhanced Weathering/OAE We would also urge the Biden Climate Team to set up a department in one of the government agencies with a title, such as Department for Enhanced Weathering and OAE, with a consulting staff consisting of many of the investigators listed in this document. This department would have a budget for initiating EW, OAE, eOAE and heOAE activities in the U.S. and possibly abroad. In addition to funding from the government, it should also be positioned to accept Carbon Tax funds, if they ever become available. The Department of Energy currently has a Department of Fossil Energy and Carbon Management which could perform these functions. However, their current strong focus is on DACS. A department more focused on EW/OAE might be advisable. NOAAs Ocean Acidification Program (OAP) would be the place to handle OAE, eOAE and heOAE programs.

Carbon Tax and Enhanced Weathering There has been considerable discussion of instituting a carbon tax on all fossil fuel positioned to be used in the U.S. This has especially been advanced by the Citizen's Climate Lobby. The bills in congress to institute this have not yet been approved and may never be. They propose giving the resulting money back to U.S. Citizens. We have great concern about how long this approach would take to produce a significant decrease in carbon emissions, probably many years if at all. We also have concerns that this taxed fuel would then be used anyway and would emit CO_2 , the only difference being that the CO_2 was 'paid for.' CO_2 is still being emitted into the atmosphere. Finally, instead of giving money to citizens, where each citizen would probably receive only a small amount, it would make much more sense to use that money to support the activation of EW/OAE/eOAE/heOAE.

Other ways the Biden Team could help.

Methane Biden has addressed this issue at the COP26. Methane is a much more potent of a greenhouse gas than carbon dioxide. The concentration of methane has increased from around 700 ppb in preindustrial times to nearly 1,900 ppb by 2020. An article in *Nature* entitled Control methane to slow global warming — fast reviewed a paper by Ocko et al, 2021.

In the first 20 years after its release, methane is around **80 times more powerful as a greenhouse gas than CO₂.** It breaks down much more quickly than CO₂, with an average lifetime of around a decade, compared with centuries for CO₂. Today, satellites are part of the monitoring effort. Research shows that a relatively small number of **'super-emitters'** are responsible for a significant share of methane emissions, particularly in the oil and gas industry.

What are the major sources of methane and where are the worst offenders? Livestock is the largest source, responsible for 31% of the global total. Reducing this by putting red seaweed in cattle food is discussed on our website. **Oil and gas (O&G)** operations rank a close second. Other sources include landfills, coal mines, rice paddies, marshes, gas stoves and water-treatment plants.

Ocko et al (2021) state that global methane emissions could be cut by 57% by 2030 using existing technologies and almost one-quarter of the global methane total could be eliminated at no net cost.

The Obama administration passed rules urging the O&G industry to carefully monitor their oil wells to cut down on rogue methane emissions. The Trump administration reversed this, despite the fact that the O&G industry was opposed to this reversal. The Biden administration reversed the reversal.

Using satellites, Cusworth, et al.(2021) identified **super emitters** in the Permian Basin, the largest and fastest growing oil and gas producing region in the United States. They identified 1,100 unique and heavy sources. They state that frequent, high-resolution monitoring is necessary to accurately understand intermittent methane super emitters across large, heterogeneous O&G basins and efficiently pinpoint persistent leaks for mitigation.

The following graph from NOAA shows global methane emissions increased in 2021 by the largest amount since measurements of the greenhouse gas began in 1983 with a level of 17 parts per billion compared to 15.3 parts per billion in 2020.

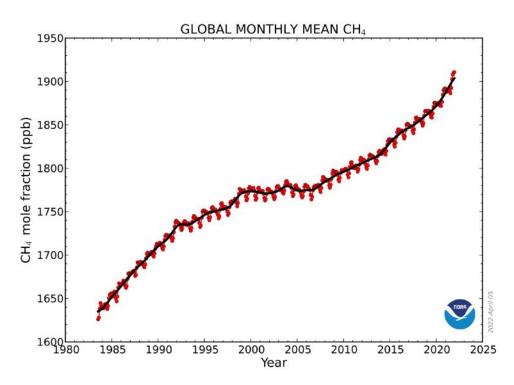
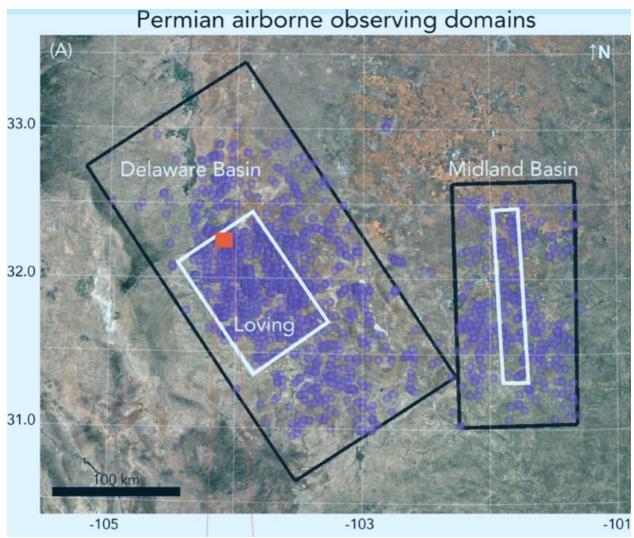


Diagram below. Domains surveyed by AVIRIS-NG and GAO during the airborne campaign from Sep-Nov 2019, covering 55,000 km² of total area, including 39,000 km² in the Delaware Basin and 16,000 km² in the Midland Basin. Black boxes represent the area surveyed at least once by the Global Airborne Observatory (GAO) instrument. White boxes represent where sites were revisited with the AVIRIS-NG instrument at least seven times during the campaign.



The Purple dots represent detected methane emission sources.

This shows the extent of the problem and the precision of the satellite monitoring. We would urge the **formation of a methane task force** to provide close monitoring of this problem and possibly penalties for emitters. Rewards for reducing emissions are built in since the O&G industry should be delighted with such a program since methane leaks controlled is money in their pockets in the form of more natural gas to sell. This task force could also work with the Department of Agriculture to develop and support the use of **food additives to cut down on the emission of methane by cattle**.

A group monitoring methane emission overseas identified methane emission sources on the west coast of Turkmenistan (Irakulis-Loitxate et al, (2021). It was **one of the largest methane emission hotspots in the world**. The same group found 29 different super emitters active in the 2017-2020 time period, 24 of them being inactive flares that are now just venting gas. We would urge the U.S. to provide assistance in halting this source of methane emission as well as monitoring gas leaks world-wide.

In other sectors, the operators of landfills, coal mines and wastewater-treatment plants could capture the gas and use it to generate electricity. And rice producers could minimize emissions with better irrigation and soil-management practices. The task force could also

monitor and assist in these activities. If these measures were implemented worldwide, projected increases in global warming could be reduced by 0.25 °C by 2050, and 0.5 °C by 2100.

Direct Air Capture of Methane. The minimum thermodynamic energy required to separate methane from ambient air is almost 5 times that of CO₂ per unit mass (Boucher and Folberth, 2010). However, expressed per t CO₂ equivalent, the minimum energy needed to separate atmospheric methane is 7 and 19 times lower than that of CO₂, considering 100- and 20-year time horizons (Jackson et al 2021). Moreover, the combustion of the recovered methane could provide 28% of the energy required for the separation (Boucher and Folberth 2010). Some zeolites and porous polymeric networks have been preliminarily identified as promising materials for methane capture because of their selectivity and sorption capacities (Jackson et al 2019, Kim et al 2013). The feasibility of deploying copper-doped zeolites to oxidize methane at atmospheric concentrations has recently been demonstrated (Brenneis et al 2021), which could render the need to develop an intermediate separation step unnecessary. Some of the zeolites effective in removing methane could also help in removing N₂O. This and other aspects of direct air capture of methane are reviewed in Cobo et al, 2022).

Hexafluoroethane (C_2F_6) The powerful greenhouse gases tetrafluoromethane and hexafluoroethane have been building up in the atmosphere from unknown sources. Modelling suggests that China's aluminum industry is a major culprit.

The gases are **thousands of times more effective than carbon dioxide at warming the atmosphere.** Official tallies of tetrafluoromethane and hexafluoroethane emissions from factories are too low to account for the levels in the air, which began to rise in 2015 after seven years of relative stability.

Seeking to pinpoint the sources of those emissions, Jooil Kim at the University of California, San Diego, and his colleagues analyzed air samples collected roughly every 2 hours between November 2007 and December 2019 on South Korea's Jeju Island. The scientists also modelled the weather patterns that transported air across the island during that period, to track the gases' origins. The results suggest that **aluminum smelters in China account for a large proportion of these chemicals in the atmosphere**. Semiconductor factories in South Korea and Japan are probably also to blame (Kim et al, 2021, and Research Highlights, Nature 596:464, 2021.

Perhaps, if China does not clear this up on their own, the U.S. government can get involved to pressure China to either stop the smelting or find alternatives to using fluorocarbons. **Refrigerant Gases** The book *Drawdown* compiled a list of 100 projects that would help combat global warming and assessed the relative impact of each. Number 1 on the list was the release of refrigerants into the atmosphere.

One kilogram (1 thousandth of a ton) of a typical refrigerant gas contributes as much to the greenhouse effect in our planet's atmosphere as two tons of carbon dioxide, **a two-thousand-fold greater effect**. One method of combating this is the development on non-greenhouse gas refrigerants. Materials called **plastic crystals** have been found to undergo huge temperature changes when subjected to small pressures near room temperature. Such materials could form the basis of safe future refrigeration technologies. (*Nature* 567:506-510, 2019). The Biden team should place fixing this problem high on their list of priorities.

A Need for Rapid Action UN Assessment Report - AR6 - Climate Change 2021 This scientific report, 3,000-plus-pages from 234 scientists, was released in August 2021 by the UN and Intergovernmental Panel on Climate Change (IPCC). They found that even if nations impose the strictest cuts to atmosphere-warming greenhouse gas emissions today, global warming is likely within the next two decades to surpass 1.5 degrees Celsius. There is wide agreement that the agreements at the COP26 fall far short of what is needed.

"The recent changes in the climate are widespread, rapid, intensifying, and unprecedented in thousands of years," said IPCC Vice Chair Ko Barrett, senior climate advisor for the U.S. National Oceanic and Atmospheric Administration. "The changes we experience will increase with further warming."

A previous U.N. climate report that examined the effects of surpassing 1.5 degrees of warming found that an additional half a degree would expose tens of millions more people to extreme heat, cause coral reefs to "mostly disappear" and result in greater habitat loss for animals that depend on Arctic summer sea ice.

Set up a UN World EW/OAE Organization analogous to the World Health Organization to supply scientific and technical support to any country needing it.

Stopping Global Warming

The finding, mining, grinding, and spreading of ultramafic rocks on croplands, noncroplands (EW) and oceans (OAE) is not technically difficult, and many countries have ultramafic deposits (see Appendix C) and many have access to the ocean. In addition to having all nations commit to stringent progressive reductions in emissions, there should also be a requirement that **each nation commit to extracting from the atmosphere an amount of CO₂ that is a significant part of their current yearly output of CO₂**. We believe that EW, OAE, eOAE and heOAE are the best ways to do this.

This approach might be called **MINE**, **GRIND**, **SPREAD** and **SEQUESTER**. Since the amount of CO_2 , a country needs to sequester would be pegged to the level of their emissions, if a country wished to free themselves of this task, this would provide a powerful inventive to further reduce emissions.

The placement of heOAE technology on all U.S. Navy nuclear powered ships would provide a huge jump start to sequester atmospheric CO₂.

We emphasize that these plans are not an excuse to stop reducing emissions. Continued reduction in emissions is critical to the success of the plan.

Fairness is an additional advantage in that each countries' contribution would be directly proportional to its level of emissions. In addition, the total cost would be distributed among all

countries, proportionate to the level of their emissions. Since it is likely that emissions will never totally reach zero, the continuation of EW, OAE, eOAE and heOAE would be necessary.

What can Individuals do? GET CREATIVE!

The following are just a few ideas.

Forming a New Industry and New Companies

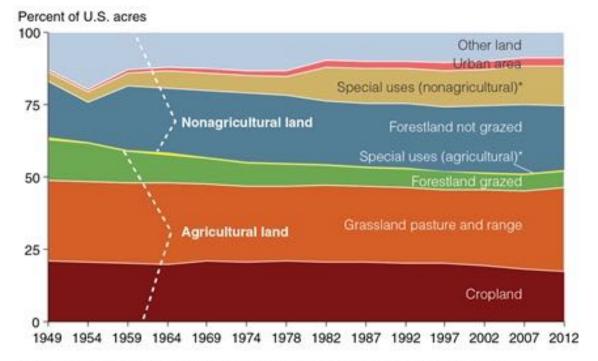
- Need to identify deposits of climate rocks.
- As shown in this document there are many of these other than olivine.
- Purchase the mining rights.
- Set up solar farms or wind farms to provide carbon free power.
- Mine and grind the climate rocks to 1um size.
- Make Climate Rocks available for both farmers and individuals worldwide.
- Apply for government subsidies.

What Climate Clubs Can Do

There are hundreds of NGO and non-profit organizations worldwide devoted to combating global warming. They have been referred to as **Climate Clubs** (Paroussos, L et al. 2019). Many of these have dozens of chapters throughout the nation and world. Combined there are many thousands of members who look on in frustrated desperation wondering what they can do other than "talk" about the problem and issue platitudes about cutting down emissions, all as the level of atmospheric CO_2 continues to rise and new catastrophic events due to climate change appear in the news almost daily. These people are desperately looking for something they personally could do that could really make a difference.

As outlined in this document, we urge an international effort to mine and grind climate rocks that permanently sequester CO₂. In addition to use by farmers or eOAE, we should make these finely ground rocks available to climate clubs throughout the world, to use on gardens, lawns, along roadways, on non-croplands and small farms, and other creative ways. with these individuals spurred on by knowing that finally what they are doing can really make a difference. "Don't just talk, do." With 8 billion people in the world, if only a fraction of them participated, this would be as commercially profitable way to sequester megatons of CO₂. This is discussed in more detail in the Addendum.

A summary of land use in the U.S. is given in the following diagram.



Share of land used for agricultural purposes has decreased 11 percent since 1949

"Special uses include rural parks and wilderness areas, rural transportation areas, defense/industrial lands (all nonagricultural uses), and farmsteads/farm roads (agricultural uses). Source: USDA, Economic Research Service calculations using data from USDA, U.S. Department of the Interior, U.S. Department of Commerce, and other sources.

The U.S. land area totals 2.3 billion acres.

There are **40 million acres of lawn in the U.S**. Climate Rocks can be mixed with the fertilizer normally used on these lawns.

In 2008 there were **45 million houses with gardens in the U.S**. These can be liberally dusted with Climate Rocks

In 2012 there were 914 million acres of farmland in the US.

Of these **414 million acres were in permanent pasture**, **389 million in cropland**. (USDA). Climate Rocks can be spread on both the pastureland and cropland. In the addendum we discuss the development of a Drone Program to assist in this.

For these clubs, instead of the slogan, "Let's plant some trees" which could backfire if they burned up or if plants shifted to respiration, the slogan should be "**let's spread Climate Rocks**" everywhere we can think of and permanently sequester carbon dioxide. It is even possible that a tax break for each ton of climate rocks an individual used, could be used to stimulate this process.

A Drone Program for Climate Based Non-profits (see above) A Program using Catamarans running on renewable energy for heOAE (see above).

Vertical Farming and Artificial Weathering Hot Spots. As outlined in the sections on hot spots, there are areas in the tropics where because of ideal temperature and moisture, weathering takes place many times faster than anywhere else on earth. This raises the possibility of **making artificial weathering hot spots in temperate countries**.

Dr. Dickson Despommier's book, *The Vertical Farm: Feeding the World in the 21st* Century, he proposes to use vertical farming in urban areas to grow food. The following figures show examples of actual vertical farms. This is now a multi-billion-dollar industry.



An existing vertical farm



An advantage of this approach is that it would be possible to use the cover to generate greenhouse type of heat, and sprinklers to provide the optimal amount of moisture. A company in Scotland called Intelligent Growth Solutions designed a vertical farm that uses artificial intelligence and specially designed power and communication technologies. The firm says this reduces energy costs by 50 per cent and labor costs by 80 per cent when compared to other indoor growing environments and can produce yields of up to 200 per cent more than that of a traditional greenhouse.

Some have complained that the need for artificial lighting to grow crops results in the use of too much energy. However, when used for EW we would not be growing crops and there would be no need for such lighting. As shown under the section on the Koornneef et al (2009) study (page 131-133), the dissolution time of 1um particles of olivine may be as short as 18 days. This would allow many rounds (up to 20) of EW to be performed each year.

The use of similar structures on large areas of land is shown in the following figure of nurseries in Oxnard California.



Acres of nurseries in Oxnard

These vertical hot spots do not have to be located on flat land, competing with cropland. As shown by this photo of solar farms in China, they can be on otherwise unused hilly areas.



The combination of providing heat, the ideal moisture, massive increases in the efficiency of a given acre of land, and rapid complete dissolution of 1um particles allowing many "crops" per year, is one example of a creative solution to rapid weathering. An additional possibility is placing solar panels on the roofs to supply the energy to run the computers that monitor the greenhouses and run heaters that could provide the option of setting the temperature inside the greenhouses to the stable temperature shown to be most effective for rapid weathering. It is conceivable that with careful monitoring of moisture and temperature it might be possible to produce hot spots that are even more efficient than the tropical ones described by Taylor et al. (2015, 2016).

Vertical EW "Farming" Research

For EW this would not be vertical farming. It is **vertical no-soil non-farming**. The expense of lights to grow crops is not needed. Its real purpose is to increase the rate of enhanced weathering for a given acre. Some vertical farming companies have claimed vertical farming is up to 350 times more efficient than flat-land farming. Several factors suggest the improvement with EW "farming" could be even greater.

As the weathering goes to completion the products are MgCO₃ (magnesite) and silica. Then the question is, how to remove these products and what to do with them? They could also be removed in a slurry and placed on OAE ships for dispersal in the ocean. An advantage of this is that it closely mimics the natural process of weathering including the products that eventually enter the ocean. This has relevance to potential governance issues about putting these products into the ocean (NAS 2021). In addition to putting, it in the ocean, Woodall et al (2021) suggested that the carbonate products of this enhanced weathering could be used to produce a cement that did not produce CO_2 .

Enhanced weathering as originally described consists of placing pulverized climate rocks on croplands. The products are then washed into rivers and into the ocean. Vertical "farming" to OAE, accelerates all aspects of the EW process. An additional advantage is that these vertical "farms" can be placed anywhere. If placed close to the mining site, this would eliminate transportation needs, one of the major expenses for EW. Since most ultramafic deposits are close the ocean, this would also cut down transportation costs for OAE. The water for the slurries does not have to be freshwater. Thus, placing the vertical farms at coastal ultramafic deposits would allow the use of salt-water slurries.

The above outlines many areas of needed research from validating the process, to designing and automating the greenhouses, calculating the amount of CO_2 such a facility could sequester, and performing economic analyses. If this approach is validated, it can be adapted by many countries.

Some economic and geologic research will be necessary to determine how much CO_2 can be sequestered by each of these "EW factories" and how much they cost. The placement of dozens of these factories around the world, next to deposits of Climate Rocks, could go a long way toward sequestering gigatons of CO_2 . For example, if each large vertical artificial EW "farm" hot spot was found to be capable of sequestering 0.5 gigatons of CO_2/yr we would only need 20 such farms around the world to sequester 10 gigatons of CO_2/yr . Countries that did not have adequate deposits of ultramafic rocks could contribute funds to support the farms in countries that did. As usual with EW the limiting factor is the amount of climate rocks that can be mined.

As noted above, the rock-inhabiting fungi *Knufia petricola* was shown to **increase olivine dissolution rates by** ~700% (Pokharel et al., 2019). By allowing the use of particles larger than 1 um this could save money if renewable energy was unable to cover all the costs of grinding to 1 um particles.

Trees

An important part of the use of vertical farms was to dramatically increase the surface area for spreading rocks over that of usual land. This raises the possibility that spraying trees could also allow the leaves to dramatically increase such surface areas. Over a fourth of all the land on earth is forestland. If this approach is a viable way to increase surface area, this would supply a large surface area for Climate Rock weathering.

A Three-way Hybrid of DACS, EW and OAE.

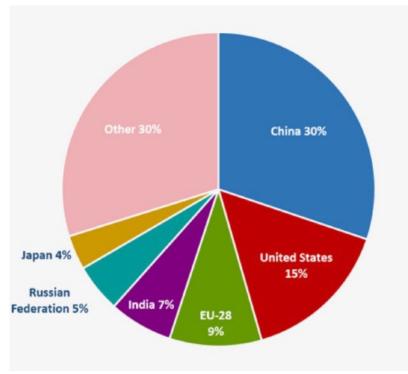
At gigaton levels leakage is a potential problem with DACS and if that leak results in many deaths it could be a death knoll for DACS. A second issue with DACS is that it does not address ocean acidification. A three-way hybrid of all three of the major NETs - DACS, EH and OAE, would solve these issues. This would involve setting up direct air capture facilities next to rivers, close to where they entered the ocean. Then instead of burying the CO_2 it would utilize vertical "farming" or a modification of it to use EW to safely sequester the CO_2 above ground. Then place the products of EW into the river to be washed into the ocean mimicking the natural EW process - voila a hybrid of DACS, EW and OAE that avoided burying CO_2 and addressed ocean acidification.

Government Subsidies

The U.S. Government has spent billions over the years in subsidies for the fossil fuel industry. As the use of fossil fuels slowly decreases due to an increase in renewable power and electric cars, the government should instead be subsidizing the **Climate Rock industry**. As companies develop the capacity to produce finely ground Climate Rocks, they should be able to apply for government subsidies to support their work and to keep the price of Climate Rocks at a level that farmers and individuals in Climate Clubs can afford it. While *in situ* sequestration could be used, it also does not address ocean acidification.

Fine Tuning the Plan

All plans require some fine tuning. The most obvious place where this **International Mine, Grind, Spread and Sequester Plan** needs fine tuning relates to the wide disparity in CO₂ emissions by different countries. The following diagram illustrates the point.



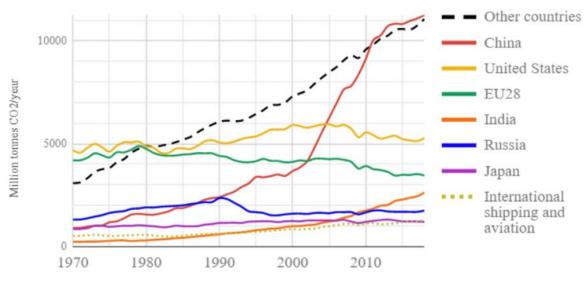
epa.gov 2015

This illustrates the well-known fact that China has the highest level of emissions at 30% and the United States the next highest at 15%. The other countries with the next highest emission rates are the EU at 9%, India 7%, Russia 5%, and Japan 4%. These ratios are similar in more recent years.

This indicates that if we require the different countries of the world to sequester a significant part of what they emit, the above countries would be responsible for approximately 70% of the total. All other countries would be responsible for sequestering only the remaining 30% of the emissions. When divided by the approximately 157 for the other countries, this leaves relatively minor amounts of sequestering required by each of those countries. It is reasonable they could form several **different groupings** dictated by which countries were geographically near each other, which had the largest deposits of mafic and ultramafic rocks, and which were next to the ocean with good ports. Some division of labor could be involved with some countries in the group supplying the rocks and doing the final grinding and still others doing the spreading on land and in the ocean such that countries with significant exposure to the ocean could specialize in OAE.

A new United Nations **World EW Organization** or **WEWO** could assist in helping to form these groupings and with scientific and technical aspects of the program.

A second relevant observation is the rate of increase in emissions in different countries. This is illustrated in the following graph.

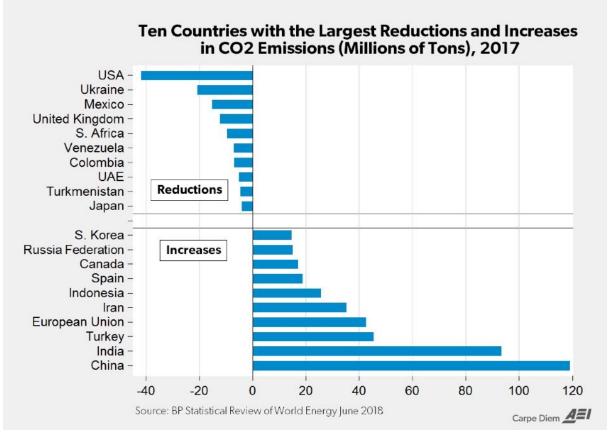


World fossil carbon dioxide emission 1970-2018

EDGAR - Emissions database for Global Atmospheric Research

This shows that the United States, EU, Russia, and Japan are showing either decreasing or stable emissions, while China has recently experienced a massive increase in emissions and the other countries as a whole are also showing a significant increase in emissions. **This supports the idea that all countries in the world need to participate in this proposal.**

Before examining what other countries could do it is useful to examine what they have done to date to reduce emissions. The following graph produced by the AEI (American Enterprise Institute) illustrates the issue.



10 Countries with the greatest reductions and increases in CO₂ emissions.

It is clear, some countries have made progress while others have not. We need to have all countries making progress by sequestering a significant part of the amount of CO_2 they each currently emit.

Do all countries have enough Climate Rocks to accomplish this? We have already learned from Goff and Lackner (1998) that there are ample deposits in the U.S. for this level of sequestration. We just need to mine them. The distribution of climate rock deposits around the world are given in Appendix C.

Russia. Will they cooperate? Because of the rapidly melting permafrost in Russia, Putin committed \$21 million to set up 140 stations to monitor the melting of permafrost. While this indicates a concern over this tipping point, it does not solve the problem. The plan proposed here will.

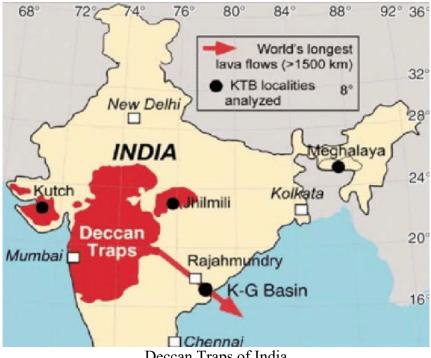
Two hundred and fifty million years ago there was such a massive amount of volcanic activity in Northern Siberia that it produced the Permian-Triassic boundary extinction event. This produced huge flows of basalt traps. The following figure shows the extent of these traps.



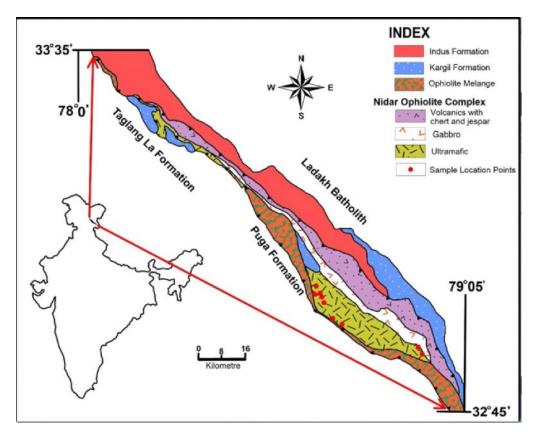
Siberian Basalt Traps

This is a massive amount of basalt. They also have ultramafic deposits. For example, Sideridiset al (2018) described significant deposits of Gabbro and Peridotites in the Urals at Alapaevsk. However, Russia's invasion of Ukraine and the resulting sanctions may result in them being less than cooperative.

India also has massive basalt deposits known as the Deccan Traps formed 66 million years ago.



Deccan Traps of India

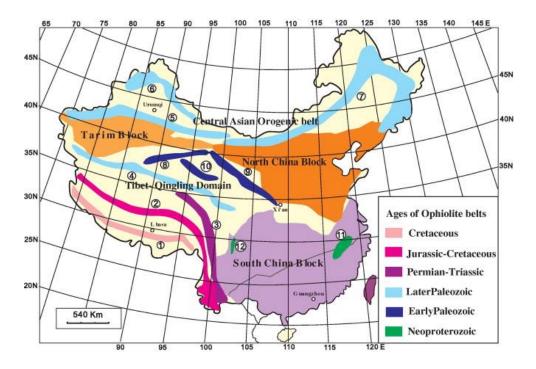


And there are also has ultramafic ophiolites in Northern India.

What about China? As shown above in the section on Ultramafics in the US, Taylor et al, (2016) summarized the larger dunite reserves in different countries. The section for China is as follows.

Country	Location	Potential Reserves*
China	Songshugou massif	33.2
	Unmeasured ultramafics	66.0
	Ophiolites	11.5
		* Gt (gigatons)

Just in these areas the total reserves are **110.7 gigatons**. If China's share of 10 gigatons/year is 3 gigatons and this required 3 gigatons of rock, this alone would last 32 years. A more comprehensive listing of ophiolites in China is shown in the following figure.



Robinson and Zhou (2008) The origin and tectonic setting of ophiolites in China.

Will China Cooperate? An extensive review of the effects of climate change in China was published by Lai in 2009. These effects were serious and widespread and included high temperatures, heavy rain and snow and severe droughts. These and others continue to the present. China has been the world's biggest investor in renewable energy over the last decade, spending nearly \$760 billion between 2010 and 2019, double the \$356 billion investment made by the U.S. Regarding wind power, the data from the China's National Energy Administration, indicate that just under 17 gigawatts of offshore wind capacity were installed in 2021. The extraordinary expansion means that China now operates almost half of the world's installed offshore wind, with 26 gigawatts of a total of 54 gigawatts worldwide.

According to the International Hydropower Association China was the world's largest producer of hydroelectricity in 2021. In 2018, hydropower generated 1,232 TWh of power, accounting for roughly 18% of China's total electricity generation. They are also leaders in solar power. China has recently committed to attaining net-zero energy by 2060 (O'Meara and Ye, 2022).

This level of destructive climate change events and a clear commitment to renewable energy, suggests they would cooperate with an international plan for mining, grinding, spreading, and sequestering CO₂ using EW and OAE.

Summaries of deposits of mafic and ultramafic rocks for the other countries are listed in Appendix C. An extensive review of all aspect of this emission is available at Crippa et al (2021) and for emissions by country by year see EDGARv6.0 FT 2020 fossil CO₂ GHG booklet 2021

The Byrd-Hagel Resolution In 1997, in response to the pending Kyoto Protocol, the Byrd-Hagel resolution was unanimously passed (95-0) by the senate. In essence it stated that the US should not sign any climate treaty that mandated reductions in emissions unless developing nations were held to similar reductions. It has constrained climate policies of subsequent administrations. The proposals outlined here would not apply since emission reductions are no longer mandatory, and all countries would be involved to a degree relative to their level of emissions.

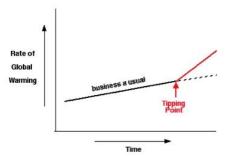
Conclusions: Advantages of the EW/OAE/eOAE/heOAE Solution to Global Warming

The above EW/OAE/eOAE/heOAE proposal would slow global warming faster than relying only on reducing emissions. We have been relying on reduced emissions for the past two decades and in that time the amount of CO₂ in the atmosphere and global warming has only increased. In addition to all the destructive aspects of global warming there are some that are quite scary. These are called tipping points. They emphasize that time is of the essence.

Tipping Points

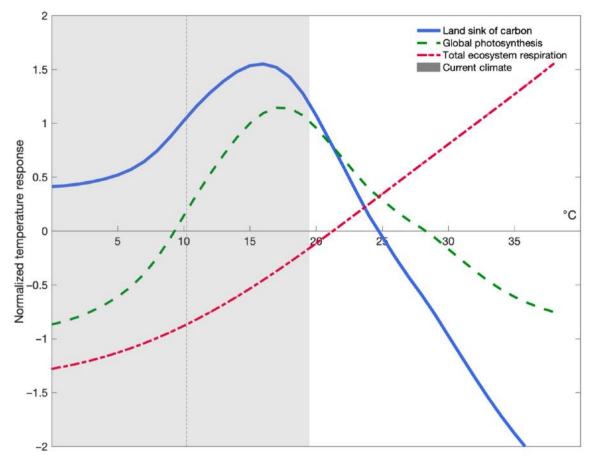
The planet is moving "perilously close to tipping points that could lead to cascading and irreversible climate impacts." (IPCC 2022). Some are already upon us.

A tipping point for global warming is a temperature at which events begin to happen that produce a positive feedback loop, accelerating further temperature rise above the previous rate. The following figure illustrates tipping point effects.



A number of tipping points have been described (Fabbri, et al 2021, Armstrong et al, 2022). Some that are really scary.

1. *Plants switch from photosynthesis to respiration.* As global temperatures increase a point is reached at which plants on earth begin to switch from photosynthesis (consuming CO_2 and producing oxygen), to respiration (consuming oxygen and producing CO_2) (Sullivan, et al (2020). Duffey et al (2021) used measurements from the largest continuous carbon monitoring network, FLUXNET to determine the temperature dependence of global rates of photosynthesis and respiration. This was based on ~1500 site years of daily data from all major biomes and plant functional types. These results are shown as follows.



Photosynthesis (green dashed line), respiration (red dashed dotted line), and a mass balance estimate of the land sink (blue solid line) in relation to current climate (gray bar) represents observed mean annual temperature range from 1991 to 2015. (Duffy et al, 2021).

This shows that globally photosynthesis (the **green line**) is decreasing, and respiration (**red line**) is increasing now (right edge of the grey field). As temperatures continue to increase this effect will increase with devastating consequences.

The photosynthetic machinery in tropical trees begins to fall at 46.7°C (117°F) (T_{crit}). Doughty et al (2023) using leaf thermocouples, pyrgeometers and remote sensing (ECOSTRESS) at multiple sites across the topics, found mid-day peak temperatures of 34°C during dry seasons with temperature tails of over 40°C and T_{crit} temperatures 0.01% of the time. They concluded that that tropical forests can only withstand an additional temperature increase of 3.9 ± 0.5 °C before reaching a potential tipping point in metabolic function. Other studies have indicated that the Amazon is starting to release more carbon than it soaks up.

2. *Melting Permafrost/burning peat*. Beneath the Arctic's frozen surface is approximately 1.5 trillion metric tons of organic carbon matter in the form of frozen soil and ancient plant matter called permafrost. As temperatures increase the *vast amounts of permafrost begin to melt* with the release of huge amounts of methane, which is 80 times more potent as a greenhouse gas than CO₂. This has already started in parts of Siberia (Shakhova, *et al.* 2010; Welch (2019); Kindy, 2021) and the Arctic.



Alaska The Permafrost is already melting EnviroNews

In addition, huge sink holes are appearing in Siberia and Alaska.



NOVA Arctic Sinkholes https:// youtu.be/ HvKpnaXYUPU

These are **due to explosive releases of methane caused by melting deep permafrost**. When permafrost carbon is released, it is oxidized to CO_2 . Thus, melting permafrost is releasing both methane and CO_2 The total contribution to greenhouse gases is equivalent to up to gigatons of CO₂. This contribution to global warming has not been included in models estimating low quickly the earth will reach the 1.5°C level.

It is estimated that there are 1.7 trillion tons of carbon as methane and CO_2 are stored beneath just the arctic. This is 250 times the amount of methane currently in the atmosphere. Thawing permafrost provides two sources of methane. That present in the surface permafrost, which is melting, and that in the deeper regions of permafrost that are also melting. In Alaska alone over 70 sites of leaking methane have been found. It is estimated that even larger amounts of methane are stored deeper underground as fossil methane, and this is also beginning to melt. (NOVA Arctic Sinkholes https:// youtu.be/ HvKpnaXYUPU).

These findings relating to tipping points already in process, emphasize the need to remove CO_2 and methane from the atmosphere as fast as possible.

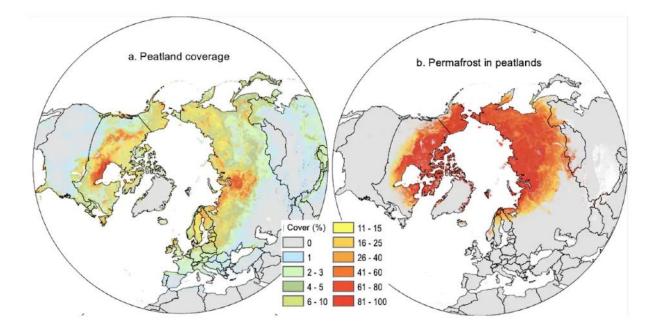
Permafrost thaw is already adding carbon dioxide and methane emissions equal to those of Japan today, at 1.1°C of warming. Even with low emissions, permafrost thaw will add carbon dioxide and methane to the atmosphere at a rate on par with human emissions from India today, totaling around 150–200 Gt CO₂ by 2100. (ICCI, 2022).

Several more recent studies further illustrate the critical nature of the problem. In a Swedish study Ramage et al (2024) reported that between 2000 and 2020 the northern permafrost region emitted 12 Tg of CO₂-C/yr, 38 Tg of CH₃-C/yr and 0.67 Tg of N₂O-N/yr. When also including lateral fluxes, the complete C and N budgets of the permafrost region result in net sources of 144 TgC/yr (including CO₂ and CH₄) 3 Tg N yr. Lateral fluxes refer to the loss of soil carbon by leaching with water (Zhang et al (2017). Methane and nitrous oxide are far more potent greenhouse gases than CO₂.

The contributions of the melting of the permafrost have not been included in climate change models. They need to be.

Peat land Peat stores huge amounts of carbon and like coal, when burned it releases large amounts of CO_2 . For example, a **peatland fire in Indonesia in 2015, produced more CO_2 in one day than the entire U.S. economy emitted in a year**.

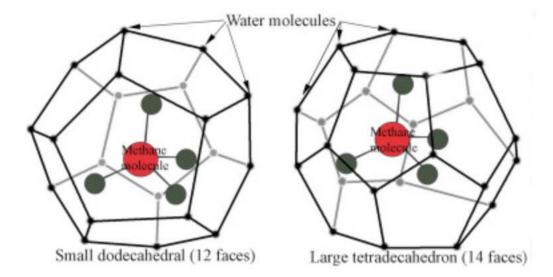
The worldwide distribution of peatland is shown on the left of the following map. Siberia and Canada predominate. Other significant areas are India and the Congo. They contain at least **twice as much carbon as all the world's forests**. The distribution of permafrost in peatlands is shown on the right.



Despite their potential, globally, peatlands are in decline with 11-15% of these ecosystems drained for grazing, agriculture, forestry, and peat mining. Barbier and Burgess (2021) concluded that protecting and **restoring peatlands can reduce global greenhouse gas emissions by about 800 million metric tons per year**, roughly equivalent to the country of Germany's annual emissions.

3. Melting Methane Hydrates

Gas Hydrates are ice like structures formed when water and low molecular weight gases such as CO₂, H₂S and methane CH₄, combine into a clathrate structure. Since methane is the primary gas involved, they are termed methane hydrates. The word clathrate is derived from the Latin *clathratus (clatratus)*, meaning 'with bars or latticed'. The following figure shows two typical methane clathrates with 46 water molecules and 12 to 14 faces.



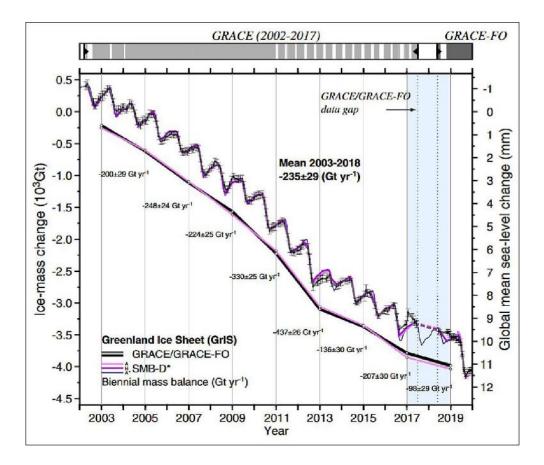
Methane clathrates are especially common along the continental shelf where they are stable at 300 to 600 meters under the surface and at the low temperatures close to the sea floor.

Worldwide it is estimated that gas hydrates contain up to **12,000 billion tons of carbon**, **more than comparable to the amount of carbon held in all fossil fuels on earth**. **This shows why it is a tipping point**. If ocean temperatures keep raising this trapped methane could be released to the atmosphere. There is evidence that this has happened before. **The Paleocene-Eocene Thermal Maximum**, **(PETM)** 55 million years ago, is believed to have been due in part to the release of many tons of methane from methane clathrates. This has been referred to as the **methane burp hypothesis**, or more technically as the **gas hydrate dissociation hypothesis**. It has been estimated that during PETM up to 1,600 gigatons of carbon were added to the atmosphere resulting in **global warming of 5 to 7 °C (41 to 45 °F)**. Recent studies suggest that while some of the C was due to a minor methane burp, most came from volcanism (Mann, 2023).

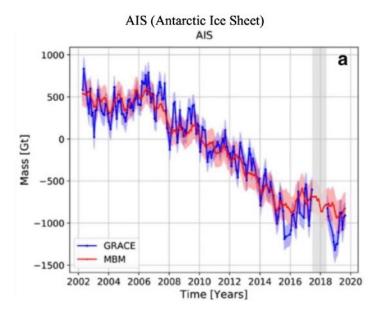
On the bright side, Ruppel and Kessler, (2017) have reviewed a number of sinks that would mitigate the amount of methane leaked to the atmosphere if methane hydrates melted. These included the anaerobic oxidation of methane by various microbes, the dissolution of methane bubbles by dissolving methane in sea water, the atmospheric oxidation of methane to CO_2 which is a less potent greenhouse gas, and others. None-the-less, the PETM, which is presumed to be due in part to **gas hydrate dissociation** illustrates the potential risk despite the sinks.

4. *Loss of albedo*. The ice in the arctic, Greenland and the Antarctic reflect large amounts of solar radiation back away from the earth cooling it. The current melting of this ice destroys this albedo effect. (Riihelä, et al (2021). This melting also leads the elevation of sea levels which in itself does not lead to positive feedback in warming while loss of albedo loss does.

The progressive melting of this ice is measured by a pair of gravity sensing satellites (GRACE). The following graph is taken from Sharing Earth Observations web site - GRACE-FO (Gravity Recovery and Climate Experiment - Follow-On) / GFO (GRACE Follow-On). The following figure shows the GRACE results for the Arctic (Greenland).



The GRACE results for Antarctica are similar.



Antarctic Sea Ice Sea ice and glaciers are two greatly different entities. This can lead to confusion about the validity of climate change. The pair of GRACE satellites weigh the total

polar ice, the vast majority of which is in glaciers and is progressively melting at both poles. In fact, **the rate of melting is massive measured in terms of 10³ gigatons or a thousand billion tons.** Sea ice by contrast constitutes as very minor part of the total polar ice, periodically melts and re-freezes and plays no role in the increasing sea levels. Ice shelf ice is also a relatively minor part of the total.

Sea ice in the Antarctic showed a slight increase in overall extent from 1979 to 2014, although some areas, such as that to the west of the Antarctic Peninsula experienced a decrease. However, after 2014, Antarctic ice extent began to decline, reaching a record low (within the 40 years of satellite data) in 2017, and remaining low since (Hobes et al, 2024; Royal Society Newsletter , 2020).

The increases in Antarctic Sea ice led to headlines such as "Antarctic Sea Ice is Increasing while the Arctic melts." This was often used by climate change deniers to claim that climate change was not a problem and that the polar ice in not melting. This is a gross misunderstanding of the true facts. **The GRACE results show how wrong that is.** Large scale loss of Arctic and Antarctic Ice is due to climate change. Freezing and thawing of sea ice is due to local weather conditions.

The International Cryosphere Climate Initiative report entitled *State of the Cryosphere* 2022 Growing Losses, Global Impacts (ICCI, 2022) has provided an excellent review of the state of the cryosphere and what we can expect in the future at different levels of emission control. Continuing at the present levels of emission would be particularly devastating.

5. Die off of phytoplankton. It is rarely appreciated that phytoplankton in the ocean sequester as much CO_2 as all the trees on land (Longhurst, et al 1995; Field, et al, 1998; Falkowski, 2012; MacRae, 2020). If these die off because of ocean acidification, deoxygenation, and other changes in ocean chemistry, this huge reservoir of carbon dioxide will be lost. In addition, phytoplankton are at the bottom of the food chain for many fish and mammals, including humans.

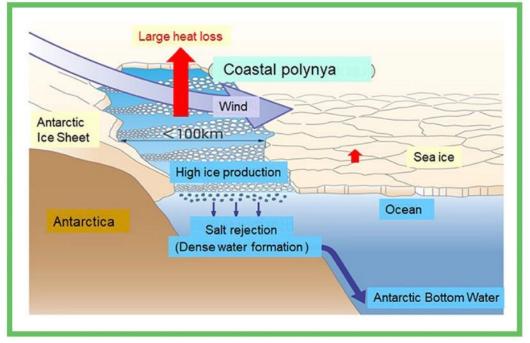
6. *Collapse of the AMOC*. The Atlantic Meridional Overturning Circulation (AMOC) consists surface and deep currents in the Atlantic Ocean It is characterized by a northward flow of warm, salty water in the upper layers of the Atlantic toward Europe, and a southward flow of colder, deep waters that are part of the thermohaline circulation.



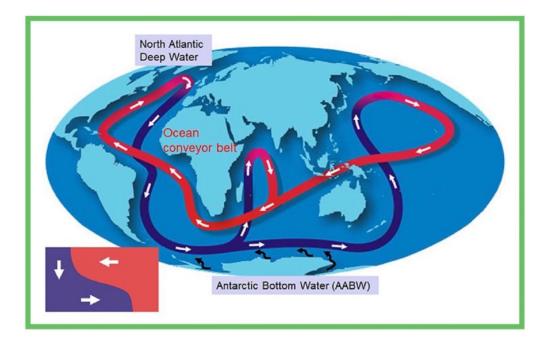
The Atlantic Meridional Overturning Circulation

The collapse of the AOMC would alter the North Atlantic air temperatures by 7°C (NIC-NIE, 2021)

7. Warming of Antarctic Bottom Water When water at the poles freezes to form sea ice the salt in the ocean water is extruded to under lying water producing very salty and very cold water that sinks forming Antarctic Bottom Water (AABW).



The extra salty, extra dense, extra cold, and very deep Antarctic Bottom Water (AABW) circulates throughout the world's oceans.

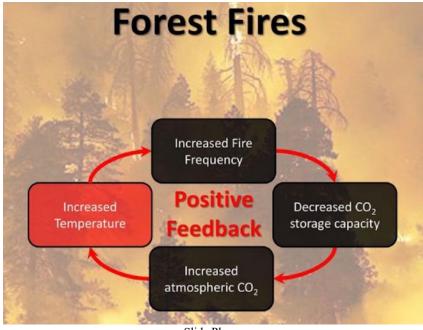


(figures from Ohshima, K and Blanckensee, S. (2023), Driving the Ocean "Pump"—Formation of Dense Water in the Antarctic. Frontiers for Young Minds. August 10),

In this way, some of the coldest water on Earth moves heat, carbon, oxygen, and other nutrients around the globe. It feeds phytoplankton, fuels ecosystems, and wields enormous influence over our climate. The problem is global warming is causing the polar ice shelves to melt and release huge amounts of freshwater into the sea. This influx causes polar water to become less salty, less dense, and thus less apt to sink. Models suggest this system my collapse by mid-century with devastating consequences (Li, Q et al, 2023). This problem is distinct from the *Collapse of the AMOC*.

8. Collapse of the WAIS (West Antarctic Ice Sheet) Another scary tipping point was reviewed by Linden, (2022). The WAIS sits on bedrock and as such is inherently unstable. Since the edge of the glacier is underwater, it is melted by warming seawater. If the amount of ice it sheds continues to exceed the amount it gains, it can set in motion a cascade of positive feedback that leads to its collapse. The Thwaites Glacier, the largest glacier in Antarctica, often called the Doomsday Glacier, is part of the WAIS. A complete collapse could raise the global sea level by 4 meters or 13 feet. Goodbye Miami and many other sea-level cities. Once ice sheet melt is accelerated due to higher temperatures, it cannot be stopped or reversed for many thousands of years, even once temperatures stabilize (ICCI 2022). Balco et al, (2023) however, suggest it may not be totally irreversible.

9. Wildfires. Forest wildfires are a clear example of a tipping point positive feedback, as shown in the following figure.



Slide Player

Global forest fires like those in Indonesia, Brazil, Central Africa, Siberia, Australia, and California, have accounted for 10-15% of all global greenhouse gas emissions (Gao et al, 2019). As global temperatures and draughts increase the risk of wildfires increases. This both increases atmospheric CO₂ levels and decreases the capacity of forests to store CO₂.

This is a tipping point that has already been in play for years.

It is estimated (van der Werf, 2017) that wildfires have emitted about **8 gigatons tons of CO₂ per year for the past 20 years**. In 2017, total global CO₂ emissions reached **32.5 gigatons** according to the International Energy Agency. As a result, **wildfires make up 5 to 10 percent of annual global CO₂ emissions each year**. The following are some specific examples of the devastating effect of wildfires on CO₂ levels.

It's estimated that the 2020 California wildfires have generated more than 91 million metric tons of CO_2 according to data from the Global Fie Emissions (GFED). That's about 25% of the annual emissions from fossil fuels in the state. Berwyn (2023) stated that the June 2023 heat extremes suggested that parts of the climate system are reaching tipping points.

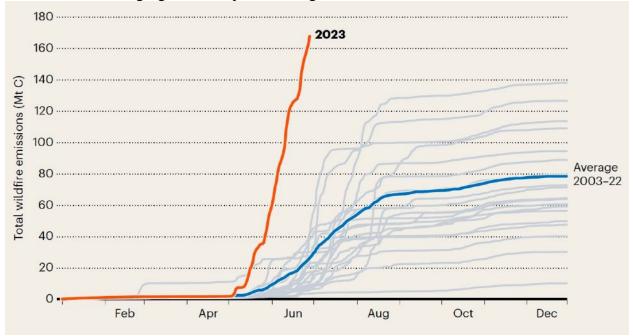
The 2020 bushfires in Australia, combined with drought conditions, released nearly twofold more carbon than what is usually emitted by fossil fuel emissions in an entire year. Even more alarming, in 2021 alone, wildfires released more than double Germany's yearly CO_2 output! In addition, it has been estimated that the air pollution caused by recent firestorms have caused 34,000 deaths.

It is likely that the only way to stop the effect of wildfires on atmospheric CO₂ levels is to return the earth temperature to preindustrial levels, a herculean task.

The following figure of the June 7, 2023, smoke in New York City because of wildfires in Canada 600 miles away, shows the wildfire problem is with us now.



An aerial view shows New York City in a haze-filled sky from the Empire State Building observatory, Wednesday, June. 7, 2023, in New York. Smoke from Canadian wildfires poured into the U.S. East Coast and Midwest on Wednesday, covering cities of both nations in an unhealthy haze, holding up flights at major airports and prompting people to fish out pandemic-era face masks. (AP Photo/Yuki Iwamura)



The following figures show just how huge those Canadian wildfires were.

The 2023 Canadian wildfires produced dramatically more CO_2 emissions than for any of the prior seasons from 2023 to 2022 (Sanderson, 2023). This is another tipping point that is happening now and an example of how quickly things can get out of control.

Global Warming causes a Dramatic Increase in Heat-related Deaths. Extreme heat is the number one weather-related cause of deaths in the U.S. and **kills more people than hurricanes, floods and tornados combined**. But in contrast to these dramatic events, people don't tend to believe that heat puts them at risk (Adams-Fuller, 2023). Burkart et al (2021)

estimated that in 2019 globally **1.69 million deaths were attributable to non-optimal temperatures**. In 2022, 61,672 heat-related deaths were recorded during a heat wave in Europe (Ballester, et al 2023). The first few days in July 2023 produced world temperatures that were the highest ever recorded. The book by Jeff Goodell (2023), *The Heat will Kill You First* outlined in detail the devastating effects of excess heat both on humans and all other living things. He also noted that since 1990 extreme heat waves amped up by climate change have **cost the global economy 16 trillion dollars.** Sun et al (2024) reported that by 2060 extreme heat waves interfering with supply chains could cost world economy **25 trillion dollars per year**.

Global Warming causes a Dramatic Increase in Draughts While it is not a tipping point, draughts due to global warming are not simply related to mean temperature. They are also related to **evapotranspiration (ETo)**, the **process by which water is transferred from the land to the atmosphere by evaporation** from the soil and other surfaces and by transpiration from plants. Atmospheric evaporative demand is a measure of the ability of the atmosphere to pull moisture from the ground. It is defined as the maximum amount of evapotranspiration that would occur, given atmospheric conditions and an unlimited supply of surface moisture.

Albano, C. et al (2022) studied changes in ETo across the Unites States from 1980 to the present. The increases in ETo across the Western United States are greater currently than 20 to 40 years ago. Temperature contributed to 57 percent of observed trends. Evaporative demand increases exponentially with increases in temperature (Chrobak, U. 2022)

The implication of these observations is that **the increase in draughts are not simply linearly related to increases in mean temperature - they are exponentially related**. This indicates **with continued global warming draughts will become progressively more severe world-wide.** This is clearly another reason to halt and reverse global warming as quickly as possible.

Mosquitos and Tics While also while not a tipping point, an additional problem with climate change is the expansion of the range of mosquitos, especially *Aedes aegypti* and *Anopheles* and tics. *Aedes aegypti* carries a slew of deadly disease including dengue, yellow fever, chikungunya and zika.

Malaria is carried by *Anopheles* mosquitos which have a unique affinity for humans. Dr. Fauci stated that any virus that can efficiently infect *Aedes aegypti* has potential access to billions of humans.

Tics carry the bacteria *Borrelia burgdorferi* which causes Lyme disease. WHO estimates that 390 million people a year are infected with dengue fever and that range is expanding. It is estimated that by 2080 60 percent of the world's population will be at risk for dengue fever. The thawing permafrost in the Arctic is releasing pathogens that have not been seen in tens of thousands of years. Goodell (2023) have reviewed these and other ways that global warming is threatening human through the range expansion of disease carrying vectors.

Carlson et al, (2022) reported that climate change will accelerate **zoonotic spillover**, a mechanistic link between global environmental change and **new disease emergence**, threatening new pandemics. Given the devastation of COVID19 this could be a serious problem.

Pandemics.

The entire world was devasted the COVID-19 pandemic, illustrating our vulnerability to virtual diseases. A meta-analysis of 375 different infectious diseases showed that 58% have at

some point been aggravated by climatic change while for 16% the effects diminished our vulnerability (Mora, et al 2022). Climate change brings people closer to pathogens. There is even the prospect that there are pathogens frozen in the melting permafrost, for which no immunity currently exists (De Olivera and Tegally, 2023).

While this is also not a tipping point, since it does not accelerate the level atmospheric CO₂, it does accelerate the effect of climate change on human health.

Air Conditioning is another tipping point-like entity in that it has a positive feedback loop. The hotter it gets the greater the need for air conditioning, and the greater the need for air conditioning to more greenhouse gases that are produced to run it. Globally, 20 percent of the total electricity used in buildings goes to air conditioning. It has been estimated that by 2050 there will be 4.5 billion air condition units. The factory in Texas that manufactures air conditioners is one of the largest factories in the world.

The existence of these and other tipping points add additional urgency to the need to quickly stop the rise in the mean earth temperature past 1.5°C. Despite COP26 many scientists believe these efforts are inadequate to prevent the earth from passing the 1.5°C point (Masood and Tollefson (2021).

Rockström, J. et al (2009, 2023) The 50+ authors from the Swedish Earth Commissions proposed a set of safe and just Earth system boundaries (ESBs) relating to climate, air pollution, phosphorus, and nitrogen contamination of water from fertilizer overuse, groundwater supplies, fresh surface water, the unbuilt natural environment, and the overall natural and human-built environment. They conclude that we have already pushed past seven out of eight scientifically established safety limits and into "the danger zone," not just for an overheating planet that's losing its natural areas, but for the well-being of people living on it. The study found "hotspots" of problem areas throughout Eastern Europe, South Asia, the Middle East, Southeast Asia, parts of Africa and much of Brazil, Mexico, China, and some of the U.S. West — much of it from climate change. The justice part of the study applies to conditions in which climate change harms people more than the planet.

They concluded that global warming beyond 1.0 °C above pre-industrial levels, which has already been exceeded, carries a moderate likelihood of triggering tipping elements, such as the collapse of the Greenland ice sheet or localized abrupt thawing of the permafrost. Above 1.5 °C or 2.0 °C, the likelihood of triggering tipping points increases too high or very high, respectively. Biosphere damage and the risk of global carbon sinks becoming carbon sources, potentially triggering further climate feedback, increase substantially. They concluded that only stabilizing at or below 1.5 °C warming avoids the most severe climate impacts on humans and other species, reinforcing the 1.5 °C guardrail set in the Paris Agreement on Climate Change. The fundamental conclusion was that the earth is quite sick now.

One fifth of the world's population lives regions that have already exceeded 1.5 °C of warming in at least one season (Jones, 2023).

The EW/OAE proposals outlined in this document provide a pathway to halting this temperature rise despite the continued emissions of CO₂. <u>In an evaluation of 12 different ocean</u> related NETs by Gattuso et al, (2021) only Enhanced Weathering and OAE were rated highest in effectiveness of carbon dioxide removal.

2023 UN Report on Risk Tipping points.

In this UNU EHS report entitled Interconnected Disaster Risks Report describes a new type of tipping point called risk tipping points. A risk tipping point is defined as the moment at which a given socioecological system is no longer able to buffer risks and provide its expected functions, after which the risk of catastrophic impacts to these systems increases substantially. These diverse cases illustrate that risk tipping points extend beyond the single domains of climate, ecosystems, society, or technology. Instead, they are inherently interconnected, and they are also closely linked to human activities and livelihoods.

They listed six.

- Accelerating extinctions
- Groundwater depletion
- Mountain glaciers melting
- Space debris
- Unbearable heat
- Uninsurable future

Systems are all around us and closely connected to us: ecosystems, food systems, water systems and more. When they deteriorate, it is typically not a simple and predictable process. Rather, instability slowly builds until suddenly a tipping point is reached and the system changes fundamentally or even collapses, with potentially catastrophic impacts. Some examples are the following.

Accelerating Extinctions. Extinction is a part of the evolutionary process that has shaped life on the planet, but often proceeds slowly over thousands to millions of years1. Unfortunately, through intense human activities such as land use change, overexploitation, climate change, pollution and introduction of invasive species, we have put our foot on the extinction accelerator. The current rate of species extinction is at least tens to hundreds of times higher than usual due to human influence, with drastic consequences for all life on our planet. Thus, with almost 1 million plant and animal species currently threatened with extinction, it is not "just" about the loss of a single species but of countless others.

Ground water depletion. More than half of the world's major aquifers are being depleted faster than they can be naturally replenished. If the water table falls below a level that existing wells can access, farmers can suddenly find themselves without the ability to access water, which puts entire food production systems at risk of failure. Some countries, such as Saudi Arabia, have already surpassed this groundwater risk tipping point; others, like India, are not far from it.

"As we indiscriminately extract our water resources, damage nature and biodiversity, and pollute both Earth and space, we are moving dangerously close to the brink of multiple risk tipping points that could destroy the very systems that our life depends on," said Dr. Zita Sebesvari, Lead Author of the report and Deputy Director of UNU-EHS. "Additionally, we also lose some of our tools and options to deal with future disaster risk." The United Nations University, Institute for Environment and Human Security (UNU-EHS) Is based in Bonn, Germany. It promotes research on risks and adaptation related to environmental hazards and global change.

Mountain Glacier Melting. On top of the world's highest mountains, glaciers act as "water towers" by storing fresh water. Meltwater from glaciers and snow supplies water for drinking, irrigation, hydropower, and ecosystems to entire regions. Due to global warming, the world's glaciers are melting at double the speed they had in the past two decades. **Between 2000 and 2019, glaciers lost 267 gigatons of ice per year.** In a warming world, we are projected to lose around 50 per cent of glaciers (excluding Greenland and Antarctica) by 2100, even if global warming can be limited to 1.5°C2.

When glaciers retreat, long-term ice storage melts and is gradually released as meltwater. Initially, the volume of water released increases until a maximum is reached, known as **peak water**. After this tipping point, glacier meltwater volume decreases as the glacier continues to shrink with effects on freshwater availability for humans and other species. 50% of world's glaciers projected to be lost by 2100 and 1.9 billion people at risk of negative effects due to glacier retreat.

Space Debris. Space debris consists of various objects, from minuscule flecks of paint to massive chunks of metal. Out of 34,260 objects tracked in orbit, only around 25 per cent are working satellites while the rest are junk, such as broken satellites or discarded rocket stages. Additionally, there are likely around 130 million pieces of debris too small to be tracked, measuring between 1 mm and 1 cm. Given that these objects travel over 25,000 kilometers per hour, even the smallest debris can cause significant damage. Each piece of debris becomes an obstacle in the orbital "highway", making it increasingly difficult for functional satellites to avoid collisions. More than 100,000 new spacecraft could be launched into orbit by 2030, compared to the approximately 8,000 we have now. Eventually, this will reach a point where one crash sets off a chain reaction, causing our orbit to become so dense with shrapnel that it becomes unusable. The existing space infrastructure would eventually be destroyed and future activities in space could become impossible.

Unbearable Heat. Human-induced climate change is causing a global rise in temperatures, leading to more frequent and intense heatwaves that will in some areas reach temperatures in which the human body can no longer survive. An *Adapt-Delay* solution would aim to counteract this risk by installing air conditioners. But this is a further drag on the electrical grid. An *Avoid-Transform* solution, on the other hand, would aim to halt the emissions of greenhouse gases and at the same time drive societal change toward low-carbon ways of living so the tipping point can ultimately be avoided. Obviously, CDR would complement Avoid and Transform.

Solutions fall into two categories: *Avoid* solutions, which target root causes and drivers of risk to avoid risk tipping points altogether, and *Adapt* solutions, which help prepare or better address the negative impacts of risk tipping points if they cannot be avoided.

For both *Avoid* and *Adapt* solutions, there are two types of actions. *Delay* actions work within the existing "business as usual" system and aim to slow down the progression toward risk tipping points or the worst impacts. But the ideal action is to *Transform*, which involves a fundamental reimagining of a system into something stronger and more sustainable than before.

Being exposed to above 35°C wet-bulb temperature for longer than six hours will result in a healthy, young, resting adult in the shade and wind suffering extreme health consequences. This threshold becomes far lower as other factors are considered, such as age, medical conditions or activity level.

Uninsurable Future. Since the 1970s, damages as a result of weather-related disasters have increased sevenfold, with 2022 alone seeing \$313 billion in global economic losses. Climate change is dramatically shifting the landscape of risks, with the number of severe and frequent disasters forecast to double globally by 2040, causing insurance prices to rise. Meanwhile, in the face of rising losses, some insurance companies in at-risk areas have decided to limit the amount or type of damages they can cover, cancel policies or leave the market altogether. Once insurance is no longer offered against certain risks (accessibility), in certain areas (availability) or at a reasonable price for homeowners (affordability), these areas are considered "uninsurable". In Australia, for example, approximately 520,940 homes are predicted to be uninsurable by 2030, primarily due to increasing flood risk.

Without the ability to access insurance, people are exposed to drastic financial losses, and may also find it difficult to buy or sell uninsurable homes, affecting the stability of housing markets. Increasingly severe hazards drive up the costs of insurance until it is no longer accessible or affordable. Once this point is passed, people are left without an economic safety net when disasters strike, opening the door to cascading socioeconomic impacts in high-risk areas

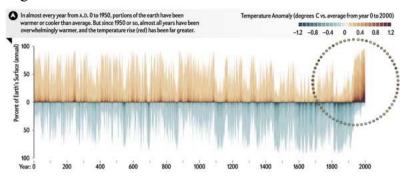
Global Warming is Real and Caused by Human Activity

A major goal of this document is to convince the U.S. and other governments, policymakers, philanthropist, billionaires, NGOs, and others of the importance of funding EW and the three OAEs, in addition to DACS, to combat global warming. However, this goal will be difficult if a significant of percentage the policymakers who have the power to activate these NETs are reluctant to do so because of active or lingering doubts about the role of humans in this crisis.

The following are some of the more frequently listed reason deniers give for their skepticism (in red) and the answers (in black).

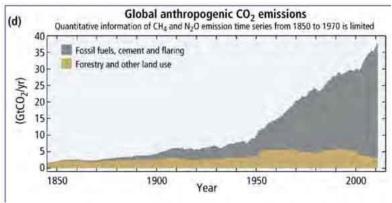
The climate has been warming and cooling for centuries.

The following diagram shows that this is true, but in recent years there has been far more warming than cooling.

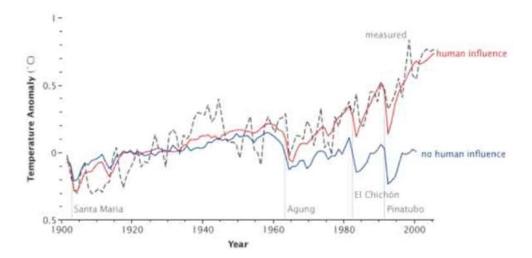


While human activity may play some role, but I don't think the science is clear on how much is man-made and how much is natural.

This is easy to sort this out. As shown in the following figure, since 1850 fossil fuels, cement use, and flaring of natural gas have been the major contributors to CO_2 emissions. It is simply a matter of adding things up based on the tons of coal, gallons of gasoline, barrels of oil, and cubic feet of natural gas burned each year, plus cubic yards of cement poured compared to pre-industrial CO_2 levels.

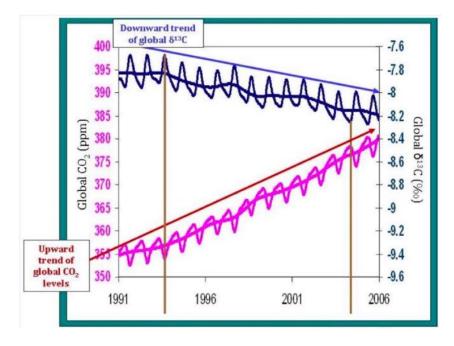


The following study came to the same conclusion. Over the past century, scientists from all over the world have been collecting data on natural factors (non-human influence) that influence climate—things like changes in the Sun's brightness, major volcanic eruptions, and cycles such as El Niño and the Pacific Decadal Oscillation. These observations (below) have failed to show any long-term natural changes that could fully account for the recent, rapid warming of Earth's temperature.



Further proof that burning fossil fuels is the source of the excess CO_2 comes from the fact that **fossil fuel CO₂ has an ID marker**. There are two stable isotopes of carbon based on the number of neutrons they contain. They are ¹³C and ¹²C. When plants take up carbon, as in CO₂, they prefer the lighter ¹²C over the heavier ¹³C. As a result, when those plants are buried and

become fossil fuels, the fossil fuels will be depleted in ¹³C compared to ¹²C. When those fossil fuels are burned, they release that C as CO₂ into the atmosphere. Since that C is depleted in ¹³C, the level of ¹³C in the atmosphere will decrease. The following figure from the Global Monitoring Laboratory, shows this is the case.



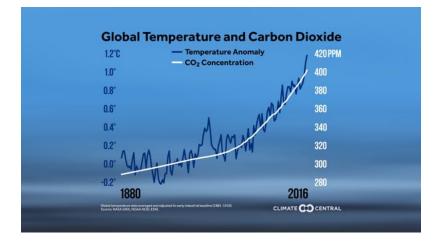
That laboratory states, "the relative proportion of ¹³C in our atmosphere is steadily decreasing over time. Before the industrial revolution, δ^{13} C of our atmosphere was approximately -6.5‰; now the value is around -8‰." This seems confusing. How can a higher number represent a lower amount of ¹³C? Note that the value is delta ¹³C not just ¹³C. This refers to the fact that the atmosphere has become more depleted in ¹³C **compared to a standard value**. **Thus, the higher the delta or difference, the greater the relative depletion**.

Climate change deniers often claim the increase CO_2 in the atmosphere comes from volcanos. The above three figures show that is not true. Volcanic ${}^{13}C/C{}^{12}$ is not decreased. Thus, when it is released, it would not result in a decrease in ${}^{13}C$ in the atmosphere. This further disproves a volcanic origin of atmospheric CO_2 .

The combination of the above three figures conclusively demonstrates that the current high levels of CO₂ in the atmosphere are primarily due to the burning of fossil fuels.

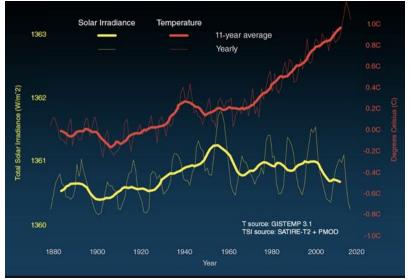
Warming may be occurring but there are many causes other than carbon dioxide.

In fact, there is a precise correlation between global warming and the level of atmospheric CO_2 . Other greenhouse gases such as methane and nitic oxide play a role, but CO_2 is the main culprit.



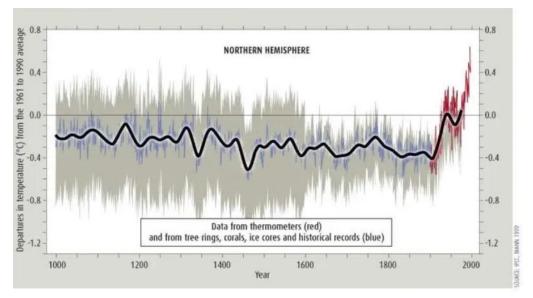
The global warming is due to the activity of the sun.

As shown below, global warming is occurring even though solar irradiance has remained relatively constant.



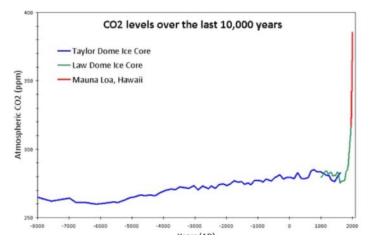
The Hockey Stick Papers. Among the most famous articles ever written about climate change were a set of two papers by Michael Mann, Raymond Bradley, and Malcolm Hughes that examined the past temperatures of earth compared to present. The first was published in Nature in 1998 (Mann et al 1998) and went back 600 years. The second was published in Geophysical Research Letters in 1999 (Mann et al 1999) going back 1,000 years. The past formed the handle and was based on data from tree rings, sediments, and other evidence. The curved stick portion was based on current temperatures. They concluded that the latter part of the 20th century showed significantly higher temperatures than all those previous years. The papers are famous because the climate change deniers went nuts trying to discredit the papers. However, multiple subsequent studies have verified the results and twenty years later the 2021 IPCC Sixth Assessment Report the handle was extended back 2,000 years and the blade of the stick rose ever higher because of continued increases in global temperature (Mann, 2023). The following is an

example of one of the many versions. The dark line is the mean temperature and the tan and red portion represent the statistical error bars.



Carbon dioxide levels have been going up and down for thousands of years.

The following figure shows that while this is somewhat the case, none of these earlier increases begin to match the magnitude the CO_2 increase since the industrial revolution.



In the Ordovician (440 Ma) Geological period CO₂ levels were 14 times higher than now, but glaciers were still present.

Crowley and Baum (1995) examined how this occurred. At that time the radiance of the sun was 4.5% lower than it is now, but computer modeling showed that alone did not explain it. At that time all the land mass was a single continent - Gondwanaland which presented some unique geographical configurations. The modeling with the decrease sun radiance and sea level Gondwanaland still did not explain it. However, when the 300–500-meter elevation of the glaciated regions was added to the model it precisely reproduced the glaciation events.

Ice sheets in the Antarctic are increasing.

This was covered in the above section on tipping points. Although in some areas and seasons, sea ice and shelf ice in Antarctica were increasing in area, the pair of GRACE satellites (Gravity Recovery and Climate Experiment), that actually weigh the total mass of ice have shown massive (billions of tons) loss of polar ice due to melting. In addition, satellite data, in addition to GRACE, showed that the Antarctic ice shelves, throughout the continent were thinning.

Many scientists do not believe that global warming is man-made.

Some scientists who work in unrelated fields may feel this way but 100% of climate scientists believe the warming is man-made.

You can't say a given heat event is due to global warming.

For a long time, this was the accepted dogma. It was even stated years ago by James Hansen, the father of climate change. However, this changed with the advent of the scientific method of **World Weather Attribution** called **severe event attribution**, spear headed by Dr. Friederike Otto (2020). Now, with climate models they could say, for example, **that climate change made the occurrence of a given event six times more probable, or even more definitively, if climate change is removed from the model, a given event would not have happened. This is done in real time.**

Global Warming is real, but it is too late to do anything about it.

The whole point of the attached documents is to show that adding Enhanced Weathering (EW) and the three types of OAE, especially heOAE, to carbon capture and sequestration efforts would provide the power needed to reverse global warming. It will not be easy. Sequestering hundreds of gigatons of atmospheric CO₂ per year is a massive job. But so was developing the atomic bomb and putting men on the moon. Both were done in less than 4 and 10 years respectively.

The above sections illustrate both the reality of global warming and the urgency needed to combat it.

Denial versus Delay

The devastating effects of global warming have eliminated all but the most diehard deniers of global warming. However, a new breed, the "delayers" have been enabled by the words net-zero. Many countries and companies have pledged to achieve net-zero by 2050. An example is Shell's commitment to net zero by 2050 and yet, at the same time, they are growing their gas business (Editorial, 2023). A similar situation involved BP. Increasing fossil fuel production while pledging net-zero is "scientifically incoherent" says James Dyke of university of Exter (Editorial, 2023)

EW/OAE/eOAE/heOAE has Economic Advantages Instead of Disadvantages.

For over two decades the countries of the world have pledged to decrease emissions and yet the level of CO_2 in the atmosphere continues to rise. Why? Because until massive renewable energy and electric cars are in place it is economically and politically costly to significantly reduce emissions leading to the resistance of many countries to meet their pledges. In addition, in some countries the mining and sale of natural resources such as coal, oil and gas, is an important

part of the economy. Eliminating this would have significant economic repercussions and lead to resistance. This point was emphasized by Thompson (2022) who stated that addressing climate change will be constrained by geopolitics and that the energy transition to renewables will be a long one.

By contrast, one of the over whelming advantages of the EW/OAE/eOAE/heOAE/in situ NETs is that they **come with an economic advantage rather than a penalty**. When you ask a country to cut emissions toward zero that is equivalent to asking them to significantly cut down on their energy supply - something that is both economically and politically disastrous. In contrast, when you ask a country to start using EW, OAE, eOAE and heOAE **it comes with economic advantages such as improved crop yields, reduction in soil acidity, expanded land suitable for agriculture, protection of fisheries by combating ocean acidification AND combating global warming by sequestering CO₂ and decreasing N₂O production on land and in the sea.** In addition, the mining industries of that country would become very profitable and if the country could produce more ultramafic rocks than they needed internally, they would enjoy an economic boon by selling the excess to other countries. This could be "the new oil." Like oil it could become a valuable tradable commodity but unlike oil it would easily pass ESG Standards. This plan would also generate new jobs worldwide. In addition, the proposals in this document would begin to control global warming before the transition to renewables was complete.

Could Save Trillions.

Based on the latest UN IPCC report (2022), to avoid catastrophic effects of climate change global emissions must peak in the next four years. To reach this goal will require an estimated \$7 trillion in investment (Andrijecic et al 2020).

World-wide EW/OAE/*eOAE*/*heOAE* proposals would save trillions of dollars in mitigation costs. We suggested that the Military set up a project to mine ultramafic rocks at Twin Sisters, WA, this could be done in tandem with a private company. Olivine Corporation which is currently mining at Twin Sisters. This is a small company and could be bought out by either the government or a private climate-oriented philanthropist.

In addition to the above trillions for investments and mitigation, the OMB reported that the **U.S. economy could lose \$2 trillion every single year** because of climate change if more isn't done to curb rising temperatures. Combating global warming by EW/OAE/*eOAE*/*heOAE* would cost less than trillions.

Ship based heOAE running on renewable energy would be the least expensive of all NETs since once the ships are paid for, the ongoing yearly costs are a fraction of those for DACS, EW, and *in situ*. Over a period of 75 years, it could save many billions (see above).

Fewer Environmentalists Objections

There have been several Direct Air Capture (DAC) initiatives, and the Biden Infrastructure Bill has included 3.5 billion dollars toward four of these projects. However, not all is rosy with this approach. For example, Summit Carbon Solutions, a 4.5 \$billion enterprise, plans to capture 12 million tons of CO_2 annually in a program to make ethanol a carbon negative fuel. The CO_2 is then transported by pipeline from Iowa and Nebraska to South Dakota where it is to be pumped a mile underground under geologic formations, presumably basalt. This sounds great but several environmental groups are opposed. " CO_2 pipelines are a questionable attempt to prop up fossil fuels by taking advantage of government subsidies while providing a pretense that they are environmentally friendly," stated Ken Winston of the Nebraska Sierra Club. There have been several other objecting voices. Also, the potential problems of storing CO₂ under basalt domes was discussed above (page 23).

We believe that EW/OAE/*eOAE*/*heOAE* will generate far fewer objections because of the many advantages inherent in the process (see above) and the absence of potentially dangerous long CO₂ pipelines and underground storage.

We emphasize that continuing to decrease emissions is a vitally important aspect of this approach. The level of commitment to sequestering CO_2 is pegged to the countries level of emissions. If they wished to reduce their level of mining, grinding, and spreading, they would need to decrease their level of emission. This could be a strong incentive to reducing emissions.

Ethical Issues

Articles have been written about the ethics of geoengineering or climate engineering (Lin, 2013; Keller et al, 2014). The main category of climate engineering is solar geoengineering or solar radiation management, which involves reflecting some sunlight back to space to limit or reverse human-caused climate change.

Carbon dioxide removal (CDR) and NETs, the practice of deliberately reducing the amount of CO₂ in the atmosphere, is often mistakenly classified with solar geoengineering as a form of climate engineering and assumed to be intrinsically risky. In fact, CDR addresses the root cause of climate change and is part of strategies to reduce net emissions. The **Intergovernmental Panel on Climate Change (IPCC) no longer refers to CDR as a subgroup of climate engineering** but **uses the terms solar radiation management and carbon dioxide removal separately** (Wikipedia, 2021).

One of the major concerns about NETs is that they may loosen the pressure to cut emissions. As we have repeatedly pointed out, this does not apply to what we propose, since continued reduction in emissions is a critical part of our proposal.

What can Donors, Philanthropists and Foundation Do?

Often foundations or individuals with means do not support combating climate change because they are not aware of specific projects where they could help. In this regard, the following Is a list of several **specific projects the foundations could fund**.

- 1. The development and support of the mining of Climate Rocks in the U.S. or other countries.
- 2. A Technical and Financial International Support Center for use of EW/OAE/eOAE/heOAE.
- 3. The design and building of Ocean Alkalinization Enhancement (OAE) and eOAE/heOAE ships run on renewable energy and using electrolysis.
- 4. Fund the development of solar or wind turbine islands supporting heOAE.
- 5. The design, building and validation of large vertical artificial hot spots.
- 6. The development of mining, processing, and using Climate Rocks in New Caledonia.

In Summary (see also Addendum)

EW, OAE, eOAE and heOAE serve as an important adjunct to the different approaches to combating climate change and global warming. They are the only NETs that can satisfy all the following issues.

1. Capable of sequestering/storage of many gigatons of CO₂ each year.

- 2. The sequestering/storage is safe and permanent.
- 3. Storage is above ground avoiding problems of below ground storge.
- 4. Improves rather than removes cropland.
- 5. Combats Ocean acidification, deoxygenation and warming.
- 6. Combats land and ocean release of N₂O and CO₂.
- 7. Does not require an energy intensive step to release CO₂, as with DACS.
- 8. At gigaton levels of sequestration/storage it is safer than DACS.
- 9. Is a method in which climate clubs, climate activists, and ordinary citizens can play an active role in the safe removal of CO₂ from the atmosphere.
- 10. EW/OAE/eOAE/heOAE could save trillions of mitigation dollars over the century.

The Logic Tree

- 1. It is universally agreed that it will be necessary to remove CO₂ from the atmosphere as well as reduce emissions.
- 2. Of the numerous NETs only EW/OAE/eOAE/heOAE satisfies the above issues.
- 3. Gigatons of Climate Rocks will be required to carry out EW/OAE/eOAE at scale.
- 4. Many countries of the world need to begin mining and grinding their deposits of climate rocks and using them for EW, OAE and *eOAE* storage
- 5. Development of heOAE could eliminate the need for ground climate rocks for OAE/eOAE.
- 5. This will require leadership from the USA government and the UN.

"What is the good of having a science good enough to make predictions if, in the end, all we're willing to do is stand around and wait for them to come true?" Sherwood Rowland Nobel Prize 1995

In the book *All We Can Save*, Naomi Klein stated, "Young people around the world are cracking open the heart of the climate crisis, speaking of a deep longing for a future they thought they had but that is disappearing each day that the adults fail to act on the reality that we are in an emergency."

Queen Elizabeth said, "They talk but don't do."

It is time to do. and We must start now.

Appendices A-C

Appendix A. Short Course in Mineralogy

Because of the wide number of minerals mentioned above the following is a short course in the relevant mineralogy.

Mafic rocks Ma = magnesium fic = ferric iron containing. Most mafic minerals are dark in color, and common rock-forming mafic minerals include olivine, pyroxene, amphibole, and biotite. Other common mafic rocks include basalt, diabase and gabbro.

Ultramafic rocks are igneous and meta-igneous rocks with a lower silica content (less than 45%), generally >18%, MgO high FeO, low potassium, and are composed of usually greater than 90% mafic minerals (dark-colored, high magnesium and iron content). The Earth's mantle is composed of ultramafic rocks.

Peridotite is a dense, coarse-grained igneous rock consisting mostly of the minerals olivine and pyroxene. Peridotite is ultramafic, as the rock contains less than 45% silica. It is high in magnesium (Mg²⁺), reflecting the high proportions of magnesium-rich olivine, with appreciable iron. The following are types of periodite (Wikipedia).

- <u>Dunite</u>: more than 90% olivine, typically with Mg/Fe ratio of about 9:1.
- <u>Wehrlite</u>: mostly composed of olivine plus clinopyroxene.
- <u>Harzburgite</u>: mostly composed of olivine plus orthopyroxene, and relatively low proportions of basaltic ingredients (because garnet and clinopyroxene are minor).
- <u>Lherzolite</u>: most common form of peridotite, mostly composed of olivine, orthopyroxene (commonly enstatite), and clinopyroxene (<u>diopside</u>) and have relatively high proportions of basaltic ingredients (garnet and clinopyroxene). Partial fusion of Iherzolite and extraction of the melt fraction can leave a solid residue of harzburgite.

Pyroxenes are a group of dark-colored rock-forming minerals found in igneous and metamorphic rocks throughout the world. They form under conditions of high temperature and/or high pressure.

Pyroxene minerals are defined by their chemical composition and crystal structure. Their generalized chemical composition is described by the formula XYZ_2O_6 where X can be Ca, Na, Fe⁺⁺, Mg, Zn, Mn or Li. Y can be Mg, Fe⁺⁺⁺, Cr, Al, Co, Mn, Sc, Ti or Vn. Z can be Si, Al or a combination of both. A wide range of cation substitutions can occur in the X and Y positions.

Augite, diopside, jadeite and spodumene are four of the best-known members of the pyroxene group; however, the pyroxene group has many other members.

Augite is a rock-forming mineral that commonly occurs in mafic and intermediate igneous rocks such as basalt, gabbro, andesite, and diorite. It is found in these rocks throughout the world, wherever they occur. Augite is also found in ultramafic rocks and in some metamorphic rocks that form under high temperatures. Augite has a chemical composition of (Ca,Na) (Mg,Fe,Al) (Si,Al)₂ O₆.

Andesite is the name used for a family of fine-grained, extrusive igneous rocks that are usually light to dark gray in color. They often weather to various shades of brown, and these specimens must be broken for proper examination.

Antigorite is a lamellated mineral in the phylosilicate serpentine with the ideal chemical formula of $(Mg,Fe^{2+})_3Si_2O_5(OH)_4$.

Aragonite is a carbonate mineral, one of the three most common naturally occurring crystal forms of calcium carbonate, CaCO₃ (the other forms being the minerals calcite and vaterite). It is formed by biological and physical processes, including precipitation from marine and freshwater environments.

Basalt is the most common rock on Earth's surface. Specimens are black in color and weather to dark green or brown. Basalt is rich in iron and magnesium and is mainly composed of olivine, pyroxene, and plagioclase. Most specimens are compact, fine-grained, and glassy. It is a dark-colored, fine-grained, igneous rock composed mainly of plagioclase and pyroxene minerals. It most commonly forms as an extrusive rock, such as a lava flow, but can also form in small intrusive bodies, such as an igneous dike or a thin sill. It has a composition similar to gabbro. The difference between basalt and gabbro is that basalt is a fine-grained rock while gabbro is a coarse-grained rock.

Diopside is a rock-forming pyroxene mineral with a chemical composition of MgCaSi₂O₆. It occurs in igneous and metamorphic rocks at many locations around the world.

Diabase The name "diabase" is used for a dark gray to black, fine-grained, intrusive igneous rock that has a composition similar to basalt and gabbro. The difference between basalt, diabase, and gabbro is in their grain size - which was determined by their cooling rates.

Diorite is the name used for a group of coarse-grained igneous rocks with a composition between that of granite and basalt. It usually occurs as large intrusions, dikes, and sills within continental crust.

Dunite is an igneous rock, of ultramafic composition, with coarse-grained texture. It is 90% olivine.

Feldspar is the name of a large group of rock-forming silicate minerals that make up over 50% of Earth's crust. They are found in igneous, metamorphic, and sedimentary rocks in all parts of the world. Feldspar minerals have very similar structures, chemical compositions, and physical properties. Common feldspars include orthoclase (KAlSi₃O₈), albite (NaAlSi₃O₈), and anorthite (CaAl₂Si₂O₈).

Fosterite is a form of white olivine rich in magnesium, with the formula Mg₂SiO₄

Harzburgite is an ultramafic variety of peridotite consisting mostly of the two minerals olivine and low-calcium pyroxene enstatite MgSiO₃ ferrosilite FeSiO₃.

Jadeite is an aluminum-rich pyroxene, while nephrite is a magnesium-rich amphibole. Both can form jade. The two minerals have very similar physical properties in the eye of the average person. The chemical composition of jadeite is NaAlSi₂O₆ or Na(Al,Fe³⁺)Si₂O₆

Lherzolite is a ultramafic rock. It is a coarse-grained rock consisting of 40 to 90% olivine along with significant orthopyroxene and lesser amounts of calcic chromium-rich clinopyroxene.

Gabbro is composed mainly of calcium-rich plagioclase feldspar (usually labradorite or bytownite) and pyroxenes (usually augite). Minor amounts of olivine might also be present in the rock.

lizardite ideal formula is $Ni_3(Si_2O_5)(OH)_4$, but most specimens contain some magnesium, and $Mg_3(Si_2O_5)(OH)_4$ is more realistic.

Olivine is the name of a group of rock-forming minerals that are typically found in mafic and ultramafic igneous rocks such as **basalt**, **gabbro**, **dunite**, **diabase**, **and peridotite**. They are usually green in color and have compositions that typically range between Mg₂SiO₄ and Fe₂SiO₄. Many people are familiar with olivine because it is the mineral of a very popular green gemstone known as peridot.

Plagioclase is the name of a group of feldspar minerals that form a solid solution series ranging from pure albite, Na(AlSi₃O₈), to pure anorthite, Ca(Al₂Si₂O₈).

Serpentinization occurs when ultramafic rocks, enriched in the minerals **olivine** and orthopyroxene, **react with water** at high temperature and are converted to rocks containing a suite of minerals dominated by serpentine. A significant by-product of the reaction is H₂.

Serpentinization encompasses **a series of hydration reactions** that occur when ultramafic rocks are exposed to circulating aqueous fluids at temperatures lower than 400°C, leading to the formation of serpentine phases. The combined formula for serpentines is:

Serpentine is a soft ductile mineral and its presence in the mantle wedge lubricates subduction of the oceanic plate. Production of serpentine in the oceanic crust produces hydrothermal fluids and releases gaseous methane and hydrogen, as observed along mid-ocean ridges. The pH of the hydrothermal fluids is generally low but under some conditions, notably at low temperature, may be high enough to be favorable to life.

The following formula shows the serpentinization for a single mineral outcome.

$$3Mg^{2+} + 2SiO_2 + 5H_2O = Mg_3Si_2O_5(OH)_4 + 6H^+$$

The following formulas show how serpentine, and olivine interact with CO₂.

$$\begin{aligned} Serpentine: &\frac{1}{3}Mg_{3}Si_{2}O_{5}(OH)_{4} + CO_{2} \rightarrow MgCO_{3} + \frac{2}{3}SiO_{2} + \frac{2}{3}H_{2}O\\ Olivine: &\frac{1}{2}Mg_{2}SiO_{4} + CO_{2} \rightarrow MgCO_{3} + \frac{1}{2}SiO_{2} \end{aligned}$$

Appendix B. Conversion Factors and Units of Measurement

What is a mole? This term is used extensively in this review. A mole is the base unit of amount of substance in the International System of Units (SI). It is defined as exactly $6.02214076 \times 10^{23}$ elementary entities, which may be atoms or molecules.

The definition of mole was adopted in November 2018 as one of the seven SI units revising the previous definition that specified one mole as the amount of substance (atoms or molecular) in 12 grams of carbon-12 where the molecular weight of C^{12} is 12. In other words, the number of atoms in a molecular weight of a substance.

This number is called the **Avogadro number**. Its value is $6.02214076 \times 10^{23}$. It was chosen so that the mass of one mole of a chemical compound in grams is numerically equal, for most practical purposes, to the average mass of one molecule of the compound in Daltons, roughly equivalent to the number of protons or neutrons in the molecule. Thus, for example, one mole of water (H₂O) contains $6.02214076 \times 10^{23}$ molecules, whose total mass is about 18 grams the molecular weight of water.

The mole is widely used in chemistry as a convenient way to express amounts of reactants and products of chemical reactions. The concentration of a solution is commonly expressed by its **molarity**, defined as the amount of dissolved substance in mole(s) per unit volume of solution, for which the unit typically used is moles per liter (mol/L), commonly abbreviated M. Wikipedia

Length

meter (m)	3.281 foot (ft)
kilometer (km ³)	0.6214 mile (mi)

Area

```
square kilometer (km<sup>2</sup>)
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0.3861 square mile (mi²)

Volume

cubic meter (m^3)	35.31 cubic foot (ft^3)			
cubic kilometer (km ³)	0.2399 cubic mile (mi ³)			

Mass

ton (metric) $1,000 \text{ kg} (0.9842 \text{ ton } \log = 2,240 \text{ lb})$ GtC gigatons of carbon $10^{12} \text{ kg carbon}$ GtCO23.7 GtCO2 = 1 GtCkilogram (kg)2.205-pound avoirdupois (lb)In 1997 the total supply of petroleum for the USA (including imports) was approximately 1 Gtper year.

TgC: teragrams of carbon or 10^{12} grams of carbon.

PgC: petagrams of carbon or 10^{15} grams of carbon; 1 PgC is equal to 1 Gigaton of carbon or 3.6 Gigatons of CO₂.

Temperature

in degrees Celsius (°C) may be converted to degrees Fahrenheit (°F) as follows: °F = $(1.8 \times °C) + 32$.

Appendix C. Worldwide Ultramafic Mining Sites and Companies

A. Companies that Provide Information on the Olivine Industry

There are several companies that provide financial analysis of the olivine industry – at a cost of thousands of dollars. Two of these are as follows.

Markets and Research.biz Global Olivine Powder and Olivine Sand Market 2021 by Manufacturers, Regions, Type and Application, Forecast to 2026 – \$3,500 Single User, \$5,250 Multi-User, \$7,000 Corporate User. This would be a source of a listing of the relevant companies. What follows is research we have done ourselves.

Global Olivine Market Research Report has In-Depth Collective analysis of different factors that analyze the Industry growth, Olivine Market Size, Share, Value, Volume. It constitutes trends, restraints, and drivers that transform the market in positive manner. The segmental analysis of Olivine Market focuses on sales, revenue and forecast by region (country), this report also states import/export consumption, supply and demand Figures, cost, price, revenue and gross margins. To get a Sample PDF of report **go to:** https://www.marketreportsworld.com/enquiry/request-sample/17332983

B. World-wide Olivine and other Ultramafics Sites by Country

The following is a list from Taylor et al (2016). It was also presented above.

Estimated Global Dunite Reserves Taylor et al, (2016)

Only the largest sites are included. For entire list see reference.

Country	Location	Potential Reserves Pg*
Australia	Owendale complex	3.7
	Tout complex	11.6
	Avondale	1.5
Canada	British Columbia	45.0
China	Songshugou massif	33.2
	Unmeasured ultramafics	66.0

	Ophiolites	11.5
Greenland	Greenland	8.2
Japan	Horoman Hill	10.5
New Zealand	Almklovdalen	7.8
Russia	Galeomean complex	17.2
	Kondyor massif	33.5
Sweden	Arutats	1.8
USA	Twin Sisters	256
	Alaska	43.9
	North Carolina & Georgia	1.6
Turkey	Ophiolites	48.0
Oman	Ophiolites	1,650
Totals	USA & Canada	346.5
	Total – Oman	601.0
	Total + Oman	2,251

* Pg (pentograms) or Gt (gigatons)

See Taylor et al (2016) Supplemental Information for references.

When harzburgite (olivine + enstatite FeSiO₃) instead of dunite was examined the reserves in Pg were much greater.

Ophiolite resources	Area (km ²)	Depth (km)	% Olivine	Est. Pg *
Cyprus				
Olympus ultramafic complex	40 ^a	2 ^b	61°	266
Samail ophiolite, Oman	14,000 ^d	5 ^d	40 ^e	64,323
Papuan Ultramafic Belt	6,000 ^f	4 ^f	71 ^f	41,763

Supplementary Table S8. Major known resources of harzburgite.

*Resources estimated using estimated areas, depths and mineralogies and specific gravities of: olivine = 3.32, orthopyroxene = 3.5, clinopyroxene = 3.3, serpentine = 2.55, spinel = 3.8¹⁷.

^aAssuming 2/3 of the 60 km² area of the Olympus ultramafic complex is harzburgite¹¹⁵.

^bDerived from Figure 3, Dilek and Eddy¹¹⁶.

^cMineralogy 61% olivine, 27.2% orthopyroxene, 4.5% clinopyroxene, 1.5% spinel, 5.4% serpentine. This is the mineralogy used by the weathering model (excluding spinel)¹¹⁷.

^dAfter Kelemen and Matter¹⁰⁴.

^eMineralogy 40% unserpentinised olivine, 40% serpentine, 10-15% orthopyroxene, 5% spinel¹⁸.

¹Mineralogy 71% olivine, 21% orthopyroxene, 6% clinopyroxene, 1% spinel, partly serpentinised¹¹⁸.

Note the large deposits in Papuan New Guinea.

United States

Eastern U.S. The extractable ultramafic rocks are in Vermont, and the Pennsylvania-Maryland-District-of-Columbia (PA-MD-DC) region, western North 'Carolina southwestern Puerto Rico. The ultramafic rocks consist of variably serpentinized dunite, harzburgite, and minor lherzolite generally containing antigorite and/or lizardite as the major serpentine minor phases. Larger deposits in Vermont and most deposits in North Carolina contain a core of dunite. Individual ultramafic bodies in the Appalachian Mountains areas great as 7 km^3 although typically they are $\leq 1 \text{ km}^3$. The total volume of all deposits in the eastern United States is conservatively estimated at 30 km³. In contrast, ultramafic deposits in southwestern **Puerto Rico have an estimated volume of roughly 150 km³**. The data show that the ultramafic deposits of the eastern United States and southwestern **Puerto Rico could potentially sequester many years of annual U.S. CO₂ emissions if** favorable geotechnical, engineering, and environmental conditions prevail. The ultramafic bodies they described all belong to ophiolite sequences, the most voluminous and widespread of all ultramafic deposits. Magnetic and gravity surveys are probably excellent methods to make a first-cut determination of deposit dimensions because of the relatively high magnetic properties and high density of many ultramafic deposits. Ultramafic rocks containing significant secondary carbonate minerals should be avoided because the sequestration potential of these rocks has already been tapped by natural processes.

Environmental restrictions in heavily populated areas of the Maryland-Pennsylvania region may impede exploitation of some serpentinite deposits. Descriptions of individual quarry sites follow.

Hunter (1941) previously calculated the mass of commercial dunite deposits in western North Carolina and adjacent Georgia. He determined a total mass of 208 x 10⁶ metric tons of relatively unaltered olivine containing more than 45 wt % MgO and a mass of 908 x 10⁶ metric tons of partly serpentinized dunite composed.

The **Belvidere Mountain** ultramafic body in Vermont, having an estimated volume of roughly 2.75 km³, can handle the equivalent of 200 years of CO_2 emissions for a United States population center of 1 million people. Belvidere Mountain in northern Vermont is the site of one of the oldest and one of the largest asbestos producing mines in the United States. The asbestos at Belvidere, which is chrysotile, was first discovered in 1896, and the site saw intermittent production until the 1920s.

Tailings at the mine consist of three main tailings piles, corresponding to the Eden, Lowell, and C-Area quarries (see below).



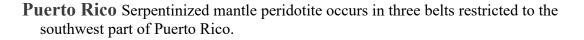
C-Area tailings pile at Belvidere Mountain, Vt. Photograph taken by Krevor et.al (2009). It is estimated that more than 29–30 million tons of serpentine tailings are located at the site.

The volumes of serpentinite in the PA-MD-DC region (roughly 30 km³) could sequester the CO, emissions of an equivalent population center for 1,600 years.

The high-purity dunite from bodies in Vermont and western North Carolina and the low-grade serpentinites of Puerto Rico (below) are more desirable than the metamorphosed serpentinites that occur throughout most of the Appalachians.

North Carolina Olivine occurs as isolated dunite bodies, or alpine-type peridotites, in the Blue Ridge. Two main districts, the **Webster-Balsam district** in Jackson County and the **Spruce Pine district** in Yancey and Mitchell counties, have produced most of the olivine. The deposits contain 50 to 90 percent olivine. Vermiculite and anthophyllite asbestos also occur in the same rocks as the olivine and have been mined in the past. North Carolina leads the nation in olivine production, although production is presently limited to the **Daybrook Mine near Burnsville** in Yancey County. Olivine production has declined in recent years because of a decline in steel production and because of increased competition from olivine imports.

Maine The **Boil Mountain ophiolite complex** is located to the west of Hurricane Mountain, north of Augusta Maine (Van Vleck and Beane, 2001). The ultramafic units consists chiefly of pyroxenite. It is not rich in olivine.

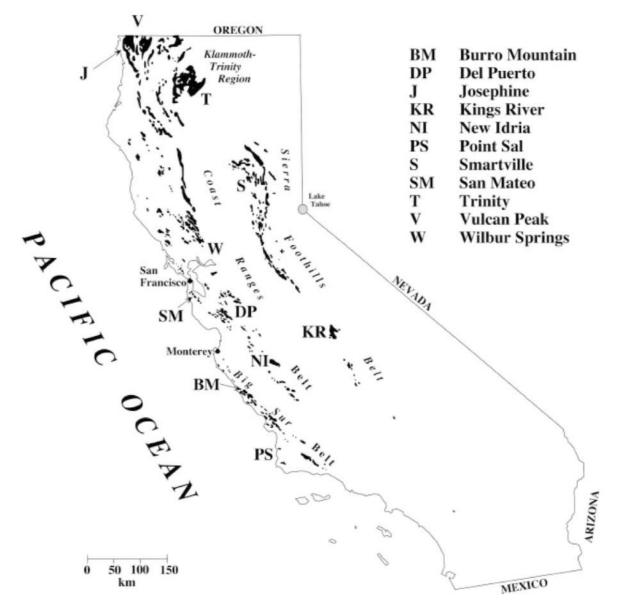




Map of the serpentinized peridotite in Puerto Rico.

Ultramafic deposits in southwestern Puerto Rico consist of serpentinized dunite and harzburgite. Because the population of Puerto Rico is about 4 million, this body could sequester the waste CO₂ of the island for more than 1,900 years. The Monte del Estado serpentinite could dispose of the CO₂ emissions produced by a million people consuming energy at current U.S. rates for 7,300 years, if such a thick body could be totally exploited. Samples from Puerto Rico and California are comparable in general appearance to each other but look quite different from the serpentinites of the PA-MD-DC region.

Western U.S. (Goff et al, 2000; Golf and Lackner, 1998; Golf et al, 1997). California (Golf and Lackner, 1998)



The following figure shows the location of ultramafic rocks in California.

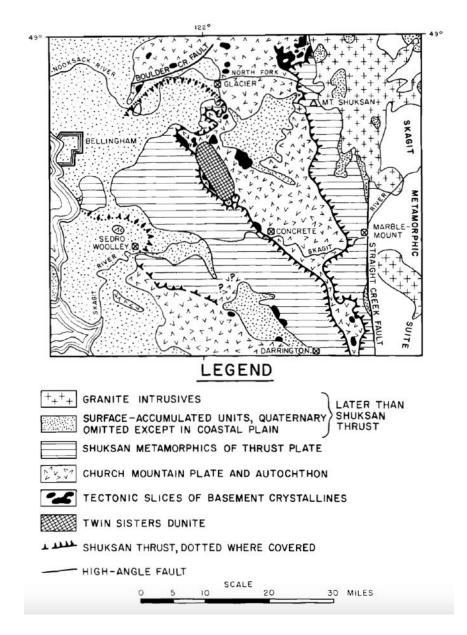
Map of California showing locations of ultramafic provinces. The Vulcan Peak peridotite in extreme southern Oregon is actually part of **the greater Josephine ophiolite**, **the largest in North America**.

Del Puerto The Del Puerto ultramafic body lies 60 km due east of San Jose in the California Coast Ranges. The body is part of an elongate slab of ophiolite whose ultramafic part (**up to 300 m thick and about 40 km**²) is variably serpentinized. The magnesite has been largely mined out. The serpentinite is the preserved base of an extensive, north-trending sheet of ophiolite that is about 50 km long and averages 2 to 6 km wide. The

thickness of the deposit varies from a few tens of meters on the west to several hundred meters on the east. Historic and dilapidated mining infrastructure is visible over all of the Del Puerto body.

Wilbur Springs Serpentinite Wilbur Springs serpentinite mass is located about 200 km NNE of San Francisco on the eastern side of the Coast Ranges. The serpentinite is the preserved base of an extensive, north-trending sheet of ophiolite that is about 50 km long and averages 2 to 6 km wide. The thickness of the deposit varies from a few tens of meters on the west to several hundred meters on the east. Wilbur Springs proper is a small but thriving hot spring resort first developed before the turn of the century. The resort now caters to people who seek quiet, natural surroundings. Most of the land occupied by the serpentinite belongs to the U.S. Bureau of Land Management or to a few cattle ranches.

Twin Sisters. The Twin Sisters dunite, Washington, is one of the largest fresh olivine deposits in the world and is the site of the largest olivine production operations in the United States (Ragan, 1963; Harben and Smith, 2006). Estimates have put remaining reserves of unaltered olivine at 200 gigatons (Harben and Smith, 2006). Unimin (Covia) and the Olivine Corporation are the main producers of olivine from the Twin Sisters ultramafic body, with a combined production of around 100,000 short tons per year. This dunite body covers about 90 km² and is presently mined by open-pit methods for refractory (foundry) sand.



Twin Sisters area after Christensen, 1971

Partially serpentinized peridotite and dunite in large masses (20 to 80% serpentine) are more common. Examples include the Belvidere Mountain prospect in Vermont, the **Canyon Mountain and Vulcan Peak** deposits in Oregon, the **Del Puerto and Burro Mountain** bodies of California and most peridotite in the **Stillwater Complex**. The Belvidere, Vulcan Peak, Del Puerto, and Stillwater bodies contain small zones (>= 4 km²) of relatively unaltered dunite.

Josephine Ophiolite perhaps the largest body of continuous serpentinite outcrop in the United States occurs at the Josephine Ophiolite of northwest California and Oregon, which extends over $\geq 800 \text{ km}^2$ (Harper, 1984). These deposits, although

some are huge, are mostly serpentinized harzburgite and are not as desirable as the unaltered dunites.

The following table compares the CO₂-sequestering potential of some U.S. ultramafic bodies.

	Twin Sisters, WA	Vulcan Peak, OR	Del Puerto, CA	Belvidere Mtn., VT	Wilbur Springs, CA	Baltimore Complex, MD	San Mateo, CA	Stillwater, MT
Volume-Density								
Area (km ²)	91	16	40	2.3	200	100	4?	26
Depth (km)	0.6	0.5	0.3	≤1	≥0.2	0.3	0.25	0.5
Est. Vol. (km ³)	54	8	12	2	40	30	1	13
Density (g/cm ³)	3.3	3.2	2.8	2.9	2.65	2.7	2.6	3.1
Wt-% Mg								
Peridotite	29.9	27.4	27.2	29.1	_	—	—	17.5
Serpentinite	<u> </u>	—	20.9	23.1	21.8	21.2	19.9	—
Combined	29	27	23	26	21	21	20	17
Sequestering Properties								
R(CO ₂) ^b	1.91	2.05	2.40	2.13	2.63	2.61	2.76	3.25
Mg (10^9 tons)	52.0	6.91	7.73	1.5	22.3	17.0	0.5	6.85
CO_2 (10 ⁹ tons)	94.1	12.5	14.0	2.7	40.3	30.8	0.9	12.4
USA (yr) ^c	18.8	2.50	2.80	0.55	8.05	6.15	0.18	2.48
World (yr) ^c	4.95	0.66	0.74	0.14	2.12	1.62	0.048	0.65

 $R(CO_2)$ R = mass ratio of rock processed to CO₂ sequestered. For example, at a deposit such as the Del Puerto ultramafic body, California, a ton of sequestered CO₂ would require on average mining, crushing, and dissolving 2.4 tons of ultramafic rock.

USA (yr) Percent of USA CO₂ emissions that could be sequestered by these rocks.

World (yr) Same as for USA (yr) but for the world's CO₂.

The sequestering potential of small ultramafic bodies is considerable. For example, the Belvidere Mountain ultramafic body, having an estimated volume of about 2 km³, is capable of handling the equivalent of 0.5 year of present total U.S. CO_2 emissions (about 5 gigatons/yr).

Compared with a typical coal mine, the Del Puerto deposit is quite large. By itself, the Del Puerto deposit could dispose of all of the CO_2 emissions associated with a population of 10 million people for about 70 years. Thus, it would suffice for the local region. However, to absorb the CO_2 output of the United States, **many more such mines would be needed.**

Large-scale Open-Pit Mining Open-pit mining on the scale envisioned would have profound economic and environmental impact. Precedents for open-pit mining of serpentinite presently exist at New Idria and at other mines in the California Coast Ranges (Coleman, 1996).

From another perspective, the abundance of Mg in the Earth's crust (0.035 mol-%;) it is not surprising that there should be more than enough Mg in ultramafic deposits to sequester global CO₂ emissions.

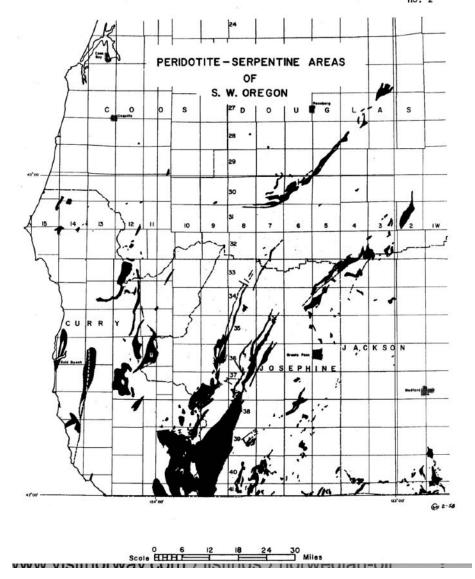
Other States: USGS article Geologic units containing Peridotite lists the

US other with ultramafic rocks – i.e., California - Kentucky - Massachusetts - Maryland - Michigan - Minnesota - New York - Oregon - Pennsylvania - Tennessee - Virginia - Vermont - Washington - Wisconsin – Wyoming. Some of these are reviewed above. Others are left to the interested reader.

Also: **Geologic units containing Ultramafic intrusive rock.** Alabama - Connecticut -Georgia - Massachusetts - Maine - Michigan - Montana - North Carolina - New Hampshire - South Carolina - Vermont - Washington - Wisconsin

Oregon (Wagner, N.S. and Ramp, L., 1958)

The following map shows the location of ultramafic deposits in Oregon.



Hawaii Though not a major emitter of CO₂, Hawaii is endowed with significant volumes of potential reservoir rocks that could be utilized to mitigate local CO 2 emissions.

Alaska Mafic and ultramafic rocks are widely distributed in the islands of the southern part of Alaska. A discontinuous, elongate zone of mafic and ultramafic plutonic rock crops out in south-central Alaska for a **distance of more than 1000 km**. **Blashke Islands** are between Juneau and Kechican. Himmelberg et al, 1986 and Himmelberg and Loney, 1995, reported on the presence of a ultramafic complex on these islands. The peridotite-gabbro suite at the Blashke Islands is one of more than **30 Alaskantype ultramafic complexes** exposed along a linear trend in southeastern Alaska. The center of the intrusion is dunite, with wehrlite, **olivine** clinopyroxenite, and gabbro occurring progressively outward. Serpentinization of the olivine-rich rocks ranges from about 25 to 75 percent. Dunite, approximately 2 km in diameter, makes up the core of the peridotite-gabbro suite and is the most abundant rock type exposed. The gabbro unit is as much as 300 m wide and forms the outermost part of the peridotite-gabbro suite. Orthopyroxene + magnetite which are commonly associated with olivine, are probably a result of a late-stage magmatic reaction:

olivine + melt = orthopyroxene + magnetite

Red Bluff Bay, southeast of Sitka, on the southeast coast of the Baranof Island, has finegrained dunite-wehrlite and clinopyroxenite form a **body 3 km by 6 km**.

Duke Island south of Kechican, has dunite, peridotite, clinopyroxenite, and hornblendite and are locally serpentinized. The dunite and peridotite in these ultramafic rocks contain small amounts of chromite, asbestos, and platinum group metals, and the clinopyroxenite locally contains accumulations of titaniferous magnetite.

This is a sampling of the ultramafic deposits in the southern part of Alaska. Himmelberg and Loney (1995) 18 sites, mostly islands, with ultramafic deposits.

So, what are Alaskan-type ultramafic complexes? Many of the igneous intrusions (plutons) are concentrically zoned, an unusual characteristic that has led to their classification as 'Alaska-type,' or 'Alaskan,' complexes (Taylor, 2016).

Are there enough ultramafic rocks in the U.S. and Puerto Rico to allow the sequestration of significant amounts of CO₂?

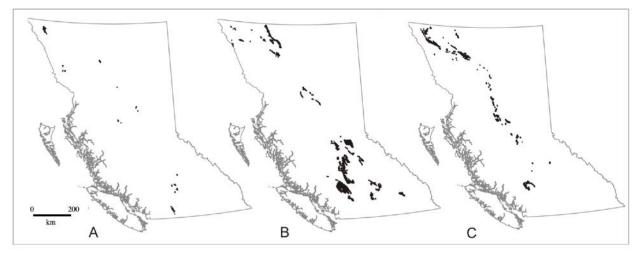
Goff & Lackner (1998) stated that small ultramafic bodies of about 1 km³, can potentially sequester about 1 gigatons of CO₂. A single large deposit of dunite (about 30 km³) could dispose of nearly 20 years of 1998 U.S. CO₂ emissions. Are there enough ultramafic deposits in the U.S. to sequester the U.S. and world contribution to global warming?

Canada

Olivine Mountain (a goldmine) consists of 3,021-hectares and covers part of the **Tulameen Ultramafic Complex**, a large slab of magnesium and iron-rich rock that ascended from near the base of the earth's crust to its current position during continental collision and the emplacement of the Cache Creek terrane in southwestern British Columbia. Dunite, olivine and hornblende clinopyroxenite are the principle ultramafic rocks (Hancock, 1991).

The Olivine Mountain Project is located in the Interior Plateau area of South-Central British Columbia, 25 kilometers northwest of Princeton near producing mines & recent major discoveries: A major recent discovery is ~50km Southeast of Westhaven Ventures (TSXV: WHN) Shovelnose Project & Kodiak Copper's (TSXV:KDK) MPD Project. GSP Resource Corp optioned a 60% Interest in Olivine Mountain Project to Full Metal Minerals Ltd. GSP Resource is located at #1610-777 Dunsmuir St., Vancouver, BC.V7Y 1K4 info@gspresource.com

Other BC Ultramafic Deposits British Columbia has favorable geology and excellent exploration potential to host the raw materials suitable for CO_2 mineral carbonation, one of the methods considered for lowering greenhouse gas levels. The following map shows the olivine and serpentine deposits separately and together.

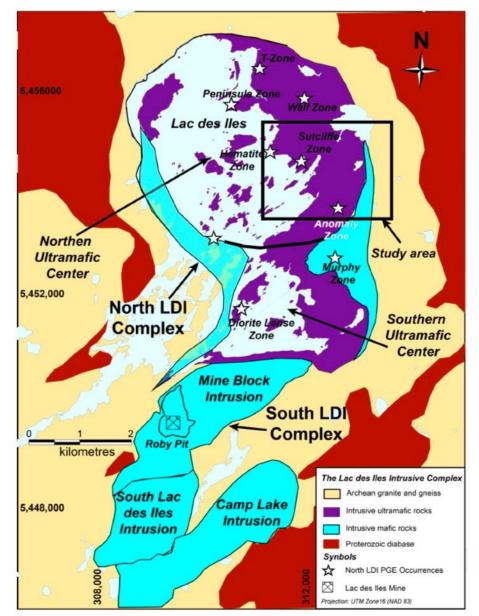


Separating out the dunite and serpentinite zones associated with ultramafic rocks: A. Areas where ultramafic rocks are reported to contain dunite only. B. Serpentinite only. C. Dunite and serpentinite are reported together. (Vooormeij and Simandl, 2004).

Abitibi Area is way north of Ottawa, immediately north of Amos. A study has been made of a **30-mile segment** of a belt of ultramafic-gabbroic igneous bodies extending past the south side of Lake Abitibi, Ontario. It is composed of peridotite and **dunite** (MacRae 1969).

Timmins Gold Mines Since the discovery of Gold in the Timmins Area, North of Toronto in Ontario, 30 different mines have produced a total of 50 million ounces of gold. Ultramafic rocks are often in close association with gold deposits. Now it is not the gold but the ultramafic rocks that is of interest. These areas deserve attention for the amount of ultramafic rocks they could produce. (Pyke, 1975).

The largest differentiated layered sill (flat intrusion of igneous rock) known in Manitoba is the **Fox River sill** This body appears to be continuous over a **length of 155 miles**. This sill as a surface area of approximately 200 square miles. Serpentinized dunite and peridotite are estimated to make up approximately 78 percent of the exposed portion of the body. The lithologic variation ranges, from serpentized dunite to gabbro, and the ratio of mafic to ultramafic rocks is approximately 1:10. This represents a massive amount of ultramafic rock.



Lac de Iles. The following figures shows the ultramafic deposits in the Lac des Iles complex in northern Ontario (Djon, 2017).

Simplified local geology map of the Lac des Iles Complex (Modified from Lavigne and Michaud, 2001)

Mining Companies in the U.S. and Canada

Cova (formerly Unimin) Corp 3 Summit Park Drive, Suite 700, Independence, **OH** 44131 Covia's facilities span North America with a **vast, convenient distribution network in** close proximity to our customers. See map on website. Our main role is to provide a broad array of high-quality minerals and material solutions for the industrial and energy markets and a comprehensive and accessible distribution network.

When you need materials in the smallest possible size, our experts can get it done. Covia's micronization services reduce minerals to the proper level to work best for your application. Whether you require large volume units or small custom packages, our individual product packaging options include a variety of bags, pails, boxes, and drums. Our high-volume bagging capabilities enable us to deliver bulk material in supersacks and totes. Covia hosts an extensive terminal network, ensuring our products are there when you need them, every time. Getting your product to you when you need it is the final step. We keep it simple.

Cova (Unimin) Corporation is a wholly owned subsidiary of global minerals company SCR. Sibelco of Belgium. Unimin operates 44 mining and mineral processing facilities in the United States, Mexico and Canada. In Mexico, the Company operates as Grupo Materias Primas de México and in Canada as Unimin Canada Ltd/Ltee. Executive offices are located in New Canaan, Connecticut with technology, analytical and sales service centers situated throughout North America. Unimin has over 2,400 employees located in 19 states in the U.S., Canada and Mexico. Industrial Customer Service 800-243-9004 <u>Sales@CoviaCorp.com</u>

Olivine Corporation is a magnesite mine located in Skagit county, Washington. It is located in Bellingham, WA, United States and is part of the Other General Purpose Machinery Manufacturing Industry. Office: 928 Thomas Rd, Bellingham, WA, 98226-9044. Phone (360) 733-3332 It is much smaller than the Cova, Corp.

Olivine Corp is located in Bellingham, Washington. This organization primarily operates in the Incinerators, Metal: Domestic or Commercial business / industry within the Industrial and Commercial Machinery and Computer Equipment sector. This organization has been operating for approximately 58 years. Olivine Corp is estimated to generate \$280,000 in annual revenues and employs approximately 2 people at this single location. The Olivine Corporation Mine is part of the San Juan Wilderness. The Olivine Corporation Mine was closed at the time of data entry with no known plans to reopen.

The Swen Larsen Quarry sits at the base of the Twin Sisters Mountain and is a key site where olivine is mined. This quarry is one of a few places in the United States known to have access to olivine (Kogel, 2006). The quarry has been in operation since 1953. Twin Sisters Olivine (formerly known as United Western Supply) has owned this site and Olivine Corporation has consulted on operations since January 27, 2012, to present time. The olivine from this site is mainly used for molding sand in metals casting, a component in refractory lining of combustion chambers, and for artistic use in the community. Current mining operations include excavation of material, crushing and screening on-site, and the hauling of material off-site for further processing and sale to market. The active season is 1 to 2 months a year.

GSP Resource Corp. (TSX-V: GSPR) is a mineral exploration & development company focused on projects located in Southwestern British Columbia. The Company has

an option to acquire a 100% interest and title to the Alwin Mine Copper-Gold-Silver Property in the Kamloops Mining Division, as well as an option to acquire 100% interest and title to the Olivine Mountain Property in the Similkameen Mining Division. For more information, please contact:

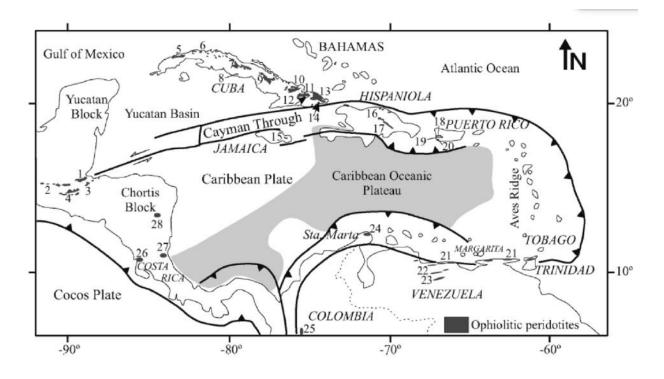
Simon Dyakowski, Chief Executive Officer & Director Tel: (604) 619-7469 Email: <u>simon@gspresource.com</u>

Full Metal Minerals Ltd. (TSX-V: FMM) was incorporated in 2003 as a public company. It is is a Canada-based mineral exploration company. The company is engaged in the acquisition, exploration, and development of resource properties. 409 Granville Street, Suite 1500, Vancouver, British Columbia V6C 1T2, Canada. <u>www.fullmetalminerals.com</u> Full Metal Minerals Proceeding with Option Agreement to Earn 60% Interest in **Olivine Mountain Project** with GSP Resources. **Contact Information -** For more information, please contact: Simon Dyakowski, Chief Executive Officer & Director Tel: (604) 619-7469 Email: simon@gspresource.com

Noble Mineral Exploration, Inc. Toronto, Ontario August 11, 2021 is pleased to announce that it has closed agreements with a number of parties (the "Parties") to option or acquire 321 mining claims (the "Claims") in **Mann, Hanna, Duff,** and **Reaume Townships**, covering an area totaling approximately 6,539 hectares. As reported by the Company on May 31, 2021, the Company has also staked an additional 256 mining claims in Mann, Hanna, Duff and Reaume Townships totaling approximately 5,453 hectares. There are over **20 km of mapped ultramafic rocks in Mann Township**. The ultramafics consist mainly of mafic sheets, sills and dikes that have intruded into and differentiated within volcanogenic sediments. The differentiated intrusions are composed of basal peridotite, usually serpentinized with a transition to pyroxenite, and then gabbro. The peridotite, and the better mineralized dunite, are the host rocks for the nickel-cobalt sulphide.

Caribbean Area

As shown in the following map, there are numerous deposits of ultramafic rocks in the Caribbean area (Lewis et al, 2006). (See this article for more references.) All the ultramafic rocks around the Caribbean have been serpentinized to at least some degree. There are three main serpentine minerals, antigorite, lizardite and chrysotile.



Distribution of **ophiolite-related ultramafic rocks** around the margins of the Caribbean Plate: 1: Sierra de Santa Cruz; 2: Baja Verapaz Unit; 3 Juan de Paz; 4: El Tambor Group (South Motagua and North Motagua); 5: Cajálbana; 6: Habana-Matanza; 7: Villa Clara; 8: Escambray; 9: Cam- agüey; 10: Holguín; 11: Mayarí-Cristal; 12: Alto de La Corea; 13: Moa-Baracoa; 14: Sierra del Convento; 15: Arntully; 16: North Coast Belt; 17: Loma Caribe; 18: Monte del Estado; 19: Río Guanajibo; 20: Bermeja; 21: La Franja Costera; 22: Loma de Hiero; 23: Villa de Cura; 24: Guajira Peninsula (serpentinites of Cabo de la Vela); 25: "Dunita de Medellín" (Aburrá ophiolite); 26: Santa Elena; 27: Rio San Juan; 28: Siuna. Main localities are numbered in italics.

Guatemala Ophiolitic rocks exposed along the Motagua Fault Zone in Guatemala include some large bodies of harzburgite such as the Sierra de Santa Cruz and La Gloria massifs. Recently have recognized four main ophiolite units containing peridotites (1) Sierra de Santa Cruz, (2) Baja Verapaz, (3) Juan de Paz, and (4) El Tambor group (South Motagua and North Motagua).

Cuba In Cuba, the largest bodies of ophiolite-related ultra-mafic rocks (serpentinized peridotites and serpentinites) crop out to the north of the island, along the so-called "northern ophiolite belt". The ophiolites of northern Cuba occur as seven separate "massifs" (ophiolite blocks) or suites exposed along the entire length of the island, from west to east: 5. Cajálbana, 6. Habana-Matanza, 7. Villa Clara, 8: Escambray 9. Camagüey, 10 Holguín, 11. Mayarí-Cristal, 12: Alto de La Corea; 13: Moa-Baracoa; 14: Sierra del Convento. All ophiolite massifs contain massive chromitite bodies, a characteristic feature of SSZ ophiolites.

Jamaica A small, faulted block of serpentinized peridotite (~0.25 km² in area) known as the 15 Arntully sepentinite is in the southern edge of the Blue Mountains along the Plantain Garden Fault in eastern Jamaica. This body is related to the Bath Dunrobin complex of basalts and gabbros which would make this an ophiolite association. The Arntully body is composed mainly of serpentinite with a core of partly serpentinized harzburgite, lherzolite, dunite and abundant blocks of rodingite.

Hispaniola Serpentinized peridotites of apparent ophiolitic affinity occur in two belts across Hispaniola, namely the 16. North Coast belt and the Median Belt in the Cordillera Central. In both belts there is evidence that these originated separately as parts of ophiolite associations that are now highly dismembered and most of the original features have been destroyed. The north coast serpentinites are small (only the Punta Gordan body exceeds 5 km across) and there is little soil developed on these. The main serpentinite belt, the 17. Loma Caribe peridotite, in central Hispaniola in the Median Belt is about 4-5 km wide and extends for 95 km from La Vega to Cerro Prieta north of Santo Domingo.

Puerto Rico in southwestern Puerto Rico there are three relatively small serpentinized peridotite bodies, namely 18. Monte del Estado, 19. Rio Guanajibo and the 20. Bermeja in the south. (see also above).

Venezuela 21. La Franja Costera with peridotites, 22. Loma de Hiero with peridotites with dunite, 23. Villa de Cura with harzburgites, 24. Guajira Peninsula (serpentinites of Cabo de la Vela).

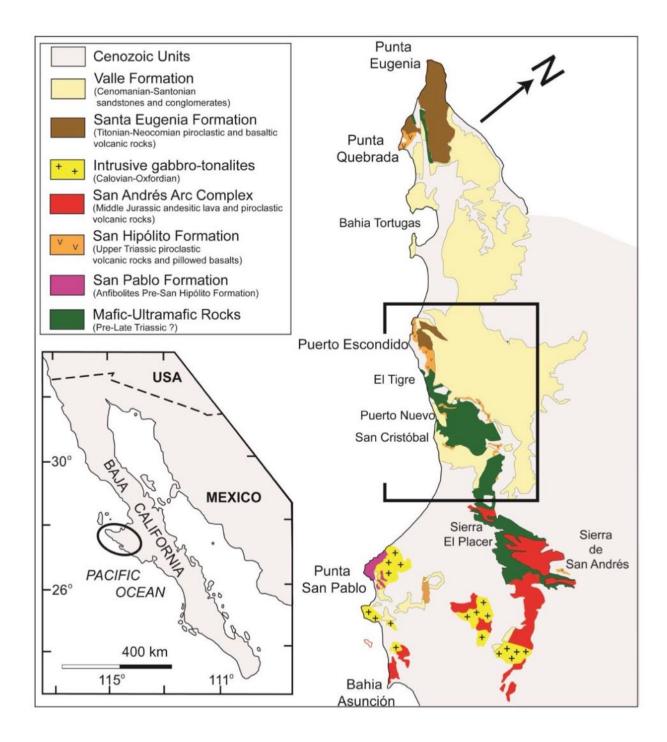
Columbia 25: "Dunita de Medellín" with Aburrá ophiolites.

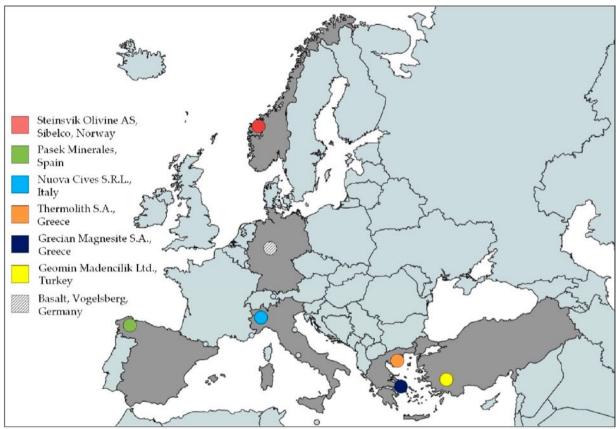
Costa Rica 26: Santa Elena with harzburgite and dunite. 27. Rio San Juan with serpentinite and Iherzolite.

Nicaragua 27. Rio San Juan and 28. Siuna with serpentinite and peridotite.

Mexico The Loma Baya deposit the ultramafic-mafic complexes in coastal Guerrero (Las Ollas, Camalotito, El Tamarindo, and Loma Baya, are associated with the Zihuatanejo terrane by the southernmost border of the Guerrero composite terrane. **There are many other locations in Mexico**. One example is shown in the map of Baja

below.





European Mining Sites and Companies (especially see Kremer et al, 2019)

Norway, Spain, Greece, Italy, and Turkey are major olivine producing countries in Europe, with a total amount of between **4,200 to 5,00 kilo tons/yr**, which represents more than 50% of the global olivine production. For details see the above reference. The companies on this map are presented by their country below.

Norway

Norway is the main source of olivine in Europe, particularly in an area stretching from Åheim to Tafjord, and from Hornindal to Flemsøy in the Sunnmøre district. There is also olivine in Eid municipality. About 50% of the world's olivine for industrial use is produced in Norway. Production is between 2,525 and 3,500 ktpa. Many deposits in the Gusdal Mine (mainly mined from Sibelco, but also from Steinsvik) is sufficient for the market.

Around 57 olivine mining sites are available in Norway (Norwegian Geological Survey, 2020), personal communication to . The biggest production comes from the Åheim district, and the mine is located close to a deep-water harbor. This site has around 92% olivine containing dunite rocks, and the purity of rock is consistent (Evans, 1997). The average composition in Gusdal mine is summarized in the table below.

Norway Gusdal Olivine Pit (Åheim Olivine

Pit), <u>Almklovdalen</u>, <u>Vanylven</u>, <u>Møre og Romsdal</u>, This site provides detailed maps to Norwegian Olivine Mining sites.

Norwegian Olivine mine, North Cape Minerals, Sibelco, AS Olivin, Raudbergvika Olivine Mine, Norddal, Møre og Romsdal, Norway

Content	Composition in olivine (%w.t)		
MgO	47		
SiO ₂	41.45		
Fe ₂ O ₃	9.2		
Cr ₂ O ₃	0.565		
Al ₂ O ₃	0.31		
NiO	0.3		
MnO	0.115		
CaO	0.12		
K ₂ O	0.01		
Na ₂ O	0.015		
LOI	1.555		

Average composition of olivine in Gusdal open mining pit, Norway. Personal communication from Norwegian Geological Survey to Vinita, R. (2020)

Steinsvik Olivine AS Velsvikvegen 729, 6133 Lauvstad, Norway welsvik@online.no

Turkey Dunite rocks and harzburgites are the main sources of olivine in Turkey. There are many deposits with a **significant amount of olivine** bearing rocks, but only a few deposits are mined to date, due to economic and location aspects.

Dudolp Mining Mimar Sinan Üsküdar-İstanbul, **Turkey** +90 850 303 3930 <u>info@dudolpmine.com</u>, <u>http://www.dudolpmine.com/</u>Dudolp Mining is a world wholesale mining supplier company specialized in natural mineral mining including olivine Oresan Mining is your reliable partner for export finance, facility investment, marketing and product development in metals, minerals and mining industries. Levent Cd. Şener Sk. No:5 Beşiktaş / İstanbul, Turkey +90 212 573 55 49 info@oresan.com

Olivine mining is considered rather new when compared with other minerals. Olivine mine has become quite important mineral in terms of its physical characteristics and in iron and steel and casting sectors of Europe's and world's developed countries for the past 20-25 years.

Eryas Mining Company – Green Sand Founded in 2008 and carrying on the activities in industrial minerals, specifically **olivine** and olivine-based refractories with the mine and the plant in Iskenderun. Ehlibeyt Mah. Ceyhun Atuf Kansu Cad. 1271.Sk., Ankara, Ankara, **Turkey** Forsterite Mg₂SiO₄ 95% Fayalite 5% Fe₂SiO₄ Website: <u>www.eryas.com</u>

Ore-Met Olivine Sands Pazaraşağı Mah. Sena Sok. No:11/10 Yalvaç / ISPARTA / Turkey +90 (246) 441 26 27

info@ore-met.com

Ore-met Mining, which was established as a family company in the region of Isparta Yalvaç in the 1970s, started its first mining experiments in 2003 with the entrepreneurial spirit of investors and administrators for institutionalization. The company, which started with barite mining, was followed by magnesite, chrome, bauxite and **ultimately olivine,** and it was established as a family partnership and today it has become a giant corporation that produces and markets mining and industrial minerals.

Produces many different types of olivine sand.

Dakduklu Minerals Established in 1982 in Isparta, Turkey Pazarasagi Mah Sena, Sok No. 11/10 Valvac, Isparta, **Turkey** <u>info@yalvacolivin.com</u> Multiple types of olivine sands

Geomin Madencilik Sanayi ve Ticaret Limited Geomin R&D Office Pamukkale University Technology Development Zone Denizli / Turkey E-Mail: info@geomin.com.tr Telephone: +90 258 215 50 30. Geomin Madencilik is a mining company working on all stages of sourcing industrial minerals for local and global markets. We supply olivine, diatomite, bentonite, bauxite, chromoium and other industrial minerals.

Egamin mining owns Rich reserves of olivine in the Denizli and Muğla regions in the southwest of Turkey. The Köyceğiz Deposit, located in Mugla, has an estimated reserve of 1,200m tons. Mimar Sinan Mahallesi, Isilar Saygin Sokak, Sevilen Apt No1/D3 Alsancak Izmir, Tyrkey

LTC Minerals Olivine gets its name from typical green olives. The aluminum foundry industry uses olivine sand to cast objects in aluminum. Olivine sand requires less water than silica sands while still holding the mold together during handling and pouring of the metal. Less water means less gas (steam) to vent from the mold as metal is poured into the mold. We supply Olivine in various sizes and specs. Please contact us for details... 1690 Sok, No: 5, D: 301 Karsiyaka – Izmir – Turkey www.ltc.com.tr +902323642462

Belgium

Euromines European Association of Mining Industries, Metal Ores & Industrial Minerals Avenue de Tervueren, 168, box 15 1150 Brussels-**Belgium**

Sibelco A global material solutions company. Our company sources, transforms and distributes specialty industrial minerals – particularly silica, clays, and **olivine**. Founded back in 1872, we have grown into a multinational business with operations in around 30 countries and an extensive multi-mineral portfolio.

SCR-Sibelco N.V. Plantin en Moretuslei 1A B-2018 Antwerp, Belgium Tel: +32 3 223 6611 Email: <u>info@sibelco.com</u> Website: <u>sibelco.com</u> Location map (pdf 833KB)

North America 3426 Toringdon Way, Suite 106, Charlotte, NC 28277 United States of America **Tel:** +1-704-625-2122 **Email:**customersupport.us@sibelco.com **Web:** sibelco.com/northamerica

Asia

Level 19, Singapore Land Tower, 50 Raffles Place, Singapore 048623 Tel: +65 6538 0355 Email:customersupport.sg@sibelco.com Web: sibelco.com/asia

Australia & New Zealand PO Box 47 Dunwich QLD 4183 Australia **Tel:** +61 7 3409 6800 **Email:** <u>info@sibelco.com</u> **Web:** sibelco.com/australia-new-zealand

South America Estrada Municipal Alcides Tofanin, s/n – Km 1,1, Jarinu, SP, 13240-000, Brazil Tel: +55 11 2398-1200 Email: <u>customersupport.br@sibelco.com</u> Web: <u>sibelco.com/south-america</u> Europe, Middle East & Africa Plantin en Moretuslei 1A, B-2018 Antwerp, Belgium Tel: +32 3 223 6611 Email:<u>https://www.sibelco.com/europe-africa-contacts/</u> Web: <u>sibelco.com/emea</u>

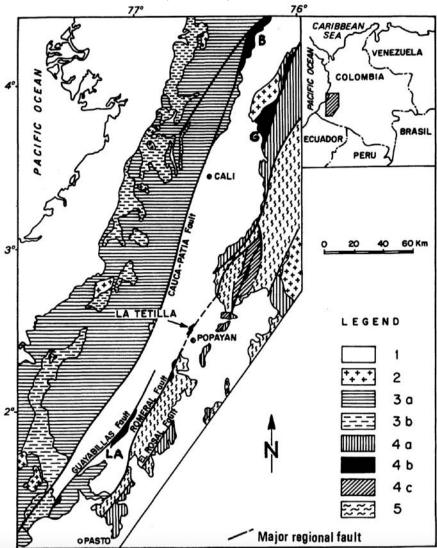
Spain

Pasek Minerales Mina Dunita Landoy, 15360 Carino, La Corna, Spain pasek@pasek.group Produces Dunites - Magnesium silicate – 37% MgO. 1,000,000 million tons/yr (This is probably an error. Should read 1,000,000 tons/yr)

Columbia

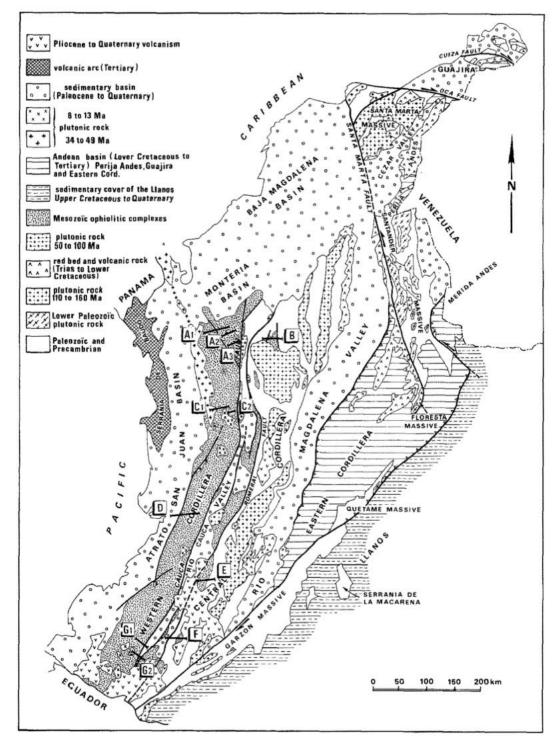
The following are two geological maps of ophiolite deposits in Columbia, both showing areas close to the Pacific. For orientation, the first shows regions just north of Cali (see above map). The first is from Spadea, P. et al.(1987) Ophiolite Complex from La Tetilla, Southwestern Colombia. The following is the legend.

Simplified geologic map of Southwestern Colombia. 1 = Quaternary-Neogene continental (volcanogenic p.p.) and marine deposits. 2 = Mesozoic intrusive. 3 = Volcanic-sedimentary complexes from Western Cordillera (Mesozoic): 3a. Basalt, chert, and terrigenous sedimentary rocks; 3b. Metasedimentary rocks. 4 = volcanic and plutonic complexes from Romeral Zone (Mesozoic): 4a. Mafic volcanism; 4b. Mafic-ultramafics: (B = Bolivar Complex; G = Ginebra Complex; LA = Los Azules Complex); 4c. High-pressure metabasites. 5 = Metamorphic and plutonic rocks from Central Cordillera (Paleozoic).



The black regions are the location of Mafic-ultramafic plutonism.

The second map is from Bourgois, J. et al (1987) Geological history of the Cretaceous ophiolitic Complexes of Northwestern South America (Colombian Andes). *Tectonophysics*. 143:307-327.



This shows that the Western Cordillera containing ophiolitic complexes runs along the Pacific Ocean from Panama to Ecuador.

Germany

Basalt Vogelsberg Active basalt quarry operated by the Vogelsberger Hartstein Industrie GMBH & Co KG of the Südhessische Aphalt-Mischwerke GmbH. Vogelsberg Basaltworks, <u>Rinderbügen</u>, <u>Büdingen</u>, <u>Wetteraukreis</u>, <u>Darmstadt</u>, <u>Hesse</u>, <u>Germany</u> Vogelsberg is a large volcanic mountain range in the German Central Uplands in the state of Hesse, separated from the Rhön Mountains by the Fulda River valley. Emerging approximately 19 million years ago, the Vogelsberg is **Central Europe's largest basalt formation**, consisting of a multitude of layers that descend from their peak in ring-shaped terraces to the base.

Italy

Nuova Cives SRL Olivine **Minerals** Localita Cross, 10080 Vidracco, **Italy** 39-0125 789078 An experience matured in over 50 years of activity in exploitation, processing and trading fields of industrial minerals that allowed to improve a specific know-how for the production of a wide range of **Olivine products**. The extracted and mined ores come mainly by national deposits –in exclusive concessions – placed in Piedmont with different mineralogical compositions and different chemical-physical characteristics.

"Bric Carlevà" Mine, mining concession covers 125 hectares and exploitable resource for more than 300 million tons of mineral.

"Finero" Mine, with an extension of more than 150 hectares and reserves for more than 250 million tons.

The mine plantation is an **open-pit** one and the mineral mined by means of explosives. The working stages are made in the modern plant of Vidracco, where it takes place the primary and secondary crushing, separation of waste materials, enrichment, tertiary and quaternary crushing, defillerization, classification. Separated and dedicated lines are presents for the production and storage of products coming from the different mines. This deposit's expected reserves contain about 100 Mt of dunites, with grades of 95% to 97% of olivine.

Olivine/dunite is mined from a deposit in the north near Turin in the municipalities of Castellamonte, Vidracco and Baldissero Canavese. This deposit's expected reserves contain about 100 Mt of dunites, with grades of 95% to 97% of olivine. The mafic-ultramafic Ivrea-Verbano Zone in Northwest Italy bears several peridotite massifs, namely Finero, Balmuccia, and Baldissero. Additionally, there are two open-pit mines currently producing: "Bric Carleva" with ~300 Mt resources and "Finero" with ~250 Mt reserves (stated by Nuova Cives SRL).

Greece

Exploration of a new Olivine Deposit in Northern Greece One of the minerals that have been exploited during the last decade in Greece is **olivine**. Today the main identified deposits of olivine in Greece are in the Vourino Mountain range in Western Macedonia, in Northern Euboea and in the central mainland. The new deposit that Grecian Magnesite intends to exploit is near the village of Chromio in Western Macedonia. The area of the deposit is about 400 x 250 meters. The deposit has a volume of 8,3 million cubic meters which corresponds to possible resources of **23.3 million tons of olivine**. Based on a systematic sampling campaign the quality is characterized as

healthy olivine. The presence of chromites adds value to olivine due to its refractory properties. A representative chemical analysis of the deposit is of the following chemistry. SiO₂ 46-48%, MgO 45-49%, CaO 1%, FeO₂ 8%, Cr2O₃ 0.2 – 1.8%.

Thermolith, S.A. P.O. Box 59, 63100 Polygyrou, Kalyves, 63100 Poligiros, Greece Telephone +30 237 1054137 Fax +30 237 1054278 <u>info@thermolith.vionet.gr</u> www.thermolith.gr

The activities of the company are the production and trade of high refractory mixes and industrial minerals (Olivine) for use in the steel production industries (steel plants). The company has very good penetration perspectives in the Balkans. Thermolith S.A. exploits important deposits of olivine, a refractory mineral used in steelmaking as slag conditioner and EBT filler sand, as well as in the manufacturing of shaped and unshaped basic refractory products. Thermolith S.A. produces a wide range of olivine-based products for steel plants. They also produce olivine in various grain sizes for the refractory industry. It is a small but dedicated company.

Rachoni Magnesite Mine, Gerakini (Chalkidiki, Northern Greece) the ultramafic rocks of the area have not only all been subjected to serpentinization, but these rocks have also undergone carbonation, silification and clay alteration (Tzamos, et al, 2020).

Grecian Magnesite, S.A. 45, Michalacopoulou str., GR 115 28 Athens, **Greece** + 30 210 7240446 -7 Email: <u>info@grecianmagnesite.com</u> As the magnesite specialists we proudly are, we offer a wide range of application-specific grades of Caustic Calcined Magnesia, Deadburned (Sintered) Magnesia, Magnesium Carbonate (Raw Magnesite) & Basic Monolithic Refractories for a host-lot of industries; from iron & steel, mining & metallurgy to manufacturing, construction, and the environment.

With more than a million tpa capacity, our Dunite production tops the global competition both in numbers and in quality. This carbon neutral and highly versatile rock is valuable in an array of applications, from blast furnace flux, foundry sand and refractories to blast cleaning, mineral wool and the environment.

Our 40-45% rich in MgO Dunite is also far less costly than any other material nearly matching its properties: dolomite, quartz sand, metallurgical slag and others. For the last several years, we have invested heavily in new Dunite based products, with large scale industrial trials both in-house and at customers sites. We are now proud to offer various Dunite products with a long list of advantages.

Today the main identified deposits of olivine in Greece are in the Vourino Mountain range in Western Macedonia, in Northern Euboea and in the central mainland. The new deposit that Grecian Magnesite intends to exploit is near the village of Chromio in Western Macedonia. The area of the deposit is about 400 x 250 meters. The deposit has a volume of 8.3 million cubic meters which corresponds to **possible resources of 23.3 million tons of olivine.**

Vitruvit S.A. Industrial Minerals Thessaloniki – Verona, 14th km Old National Road, GR 570 11, Greece

Branches in Kalives and Skoumtsa

Thermo Tap hole with optimized grain size distributions Thermo Tap hole is produced from selected mineral olivine, a refractory mineral with high percentage of Fosterite content and high refractoriness. As a result of long experience and cooperation with the steel making industry, we offer optimized grain size distributions that guarantee free and easy opening of the EBT in Electric Arc Furnaces. Standard production of EBT filler sand is 1-6mm, 2-6mm and 3-8mm.

Slag Conditioner with excellent artificial foamy slag In electric arc furnace (EAF) applications, olivine when applied as a slag conditioner promotes the development of excellent artificial foamy slag and successfully balances viscosity and volume for efficient Sulphur removal and electrode protection. Olivine is more consistent in quality and aggregate size than calcined materials and shows uniform dissolution during a heat. Standard production of Thermo slag conditioner is 10-40mm.

Olivine Sand as Foundry Sand Olivine is a valuable raw material for use in Foundries as Foundry sand for mold construction in both ferrous and non-ferrous metal casting. Foundry sand from Olivine has an uniform low thermal expansion (0,8% at 1300 °C) resulting in better casting accuracy and smoother surface. Its high heat absorption and conductivity, along with its grain-shape that leads to optimal porosity, help degassing during casting. Olivine is compatible with non-organic binders such as Bentonite, demands small quantity of water and is suitable for use in alkaline resin-bonded system. Furthermore, olivine not containing free silica, contributes to provide a high standard work environment for the workers and a high health and safety performance for the foundry.

Sandblasting Sand Particularly suitable for wet-blasting abrasive systems. Olivine is a dynamic natural mineral with high abrasion index. Having a hardness between 6.5 and 7.0 Mohs, it is suitable for restoring aluminum, fiberglass, marble/stone facades and wood as well as cleaning and providing a medium profile on steel. It is particularly suitable for wet-blasting abrasive systems, creating an enhanced and high economy slurry blast mixture that leads to advanced performance. Olivine also has the advantage of reduced disposal concerns in some cases.

Summary of Olivine Production and Potential in Part of Europe

Quarry location	Olivine production	Reserve size/amount	% Olivine content
Spain	0.7 Mt/y	n/a	25-35
Italy	0.25 Mt/y	100 Mt	90-95
Norway	2 Mt/y	6 km3; 25-30 km3; 48 km2; 250 million tons (Gusdal mine)	90-95

Vinita (2020) provided the following list of olivine production and potential in three European countries, Spain, Italy and Norway.

India

Keala, Kakkaponu Distric, India Unusual dunite: High in Mg, low in Ni

Olivine India Group 1st Floor, NM Arcade, Opp.ARRS Multiplex, Meyyanur, Salem 636009. Tamilnadu, **India**. Phone : +91-427- +91-8489913915/25 (Board Line) Email :info@olivineindia.com. Olivine Sand has been the Core Product of Olivine India Group as the name itself suggests. We host India's largest state of art manufacturing facility with **5000 Tons a month** manufacturing capacity. Olivine India is undisputed leader in Indian Market with Olivine Sand supplies to Foundries, Steel Mills, Refractory Industries and Multiple Industries for various applications.

We can manufacture up to 40 various fractions of Olivine Sand, also can customize the product as per Client's requirements.

Japan

Japan is the second-largest producer of peridotites for comparison of European olivine sources with worldwide deposits. The sample comes from the Horoman Mine in the Hidaka Province in Hokkaido.

Hokkaido In the Kamuikotan Tectonic Zone, ultrabasic rocks are found as sporadic masses in a long region of abut 300 km from northern Toikanbetsu, Teshio Province in southern Mitsuishi, Hidaka province. the zone is characterized by the association of numerous large bodies of ultrabasic itrusives

Hamada A melilite-olivine nephelinite lava flow occurring in Hamada, SW Japan

(Tatsumi et al, 1999). The nephelinite melt is multiply saturated with olivine and clinopyroxene.

Shikoku the Murotomisaki Gabbroic Complex is a still – like layered intrusion of up to 220 m in thickness and is located at Cape Muroto, Kochi Prefecture, Japan. There are several olivine – rich zones within the intrusion, which may have been formed through accumulation of olivine crystals. (Hoshide, T. et al, 2006).

China

Ophiolites are widespread and abundant in China, where they lie along suture zones delineating major tectonic blocks. They are typically tectonically disrupted mélanges composed of isolated blocks of peridotite, gabbro and basalt.

A rapidly expanding database of high-precision age dates and detailed geochemical analyses on Chinese ophiolites is providing new insight into the nature and timing of the tectonic events that shaped this part of Asia.

Oman

Semail Ophiolite, Oman 1.4 x 10⁵ gigatons Deposit Lifetime 1,056 yrs.

New Zealand

Red Hill, New Zealand 871 gigatons olivine est. Deposit lifetime 6.6 yr The Red Hills ultramafic massif, the South Island, New Zealand, contains a suite of cmscale shear zones that are composed of dunite, pyroxenite, and olivine websterite.

Dun Mountain is composed of dunite, orthopyroxene peridotite, and serpentinite. Dun Mountain is composed of dunite, orthopyroxene peridotite, and serpentinite. Dun Mountain is a mountain in the Richmond Range near the city of Nelson in the Tasman District of New Zealand's South Island. The mountain is named for its brown (Dun) color. The color is caused by the ultramafic rock which forms the mountain.

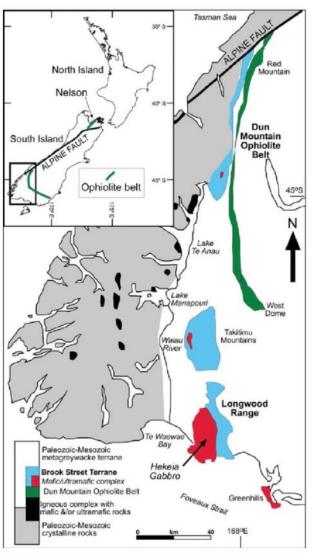


Fig 1 in Craw et al (2016)

Red Mountain area includes a portion of the Dun Mountain Ophiolite Belt, a linear feature which is exposed for at least 170 km in the southern part of South Island New Zealand. The Dun Mountain belt occurs as a series of melanges and tectonic slices with complex structural relationships between mafic and ultramafic lithologies. In contrast, the Red Mountain area comprises a relatively coherent ophiolite sequence in fault contact with surrounding metasedimentary and metavolcanic units.

Russia

JSC North Urals Dunites is planning to mine dunite as a source of olivine from the Iovinsky deposit in Russia's Ural Mountains, which promises to be the world's second largest project of its kind. Vladislav Vorotnikov, IM Correspondent, discovers how the company is dealing with environmental opposition and the challenge of finding new markets. Mount Konzhak, the site of NUD's proposed Iovinsky dunite mine, is located in

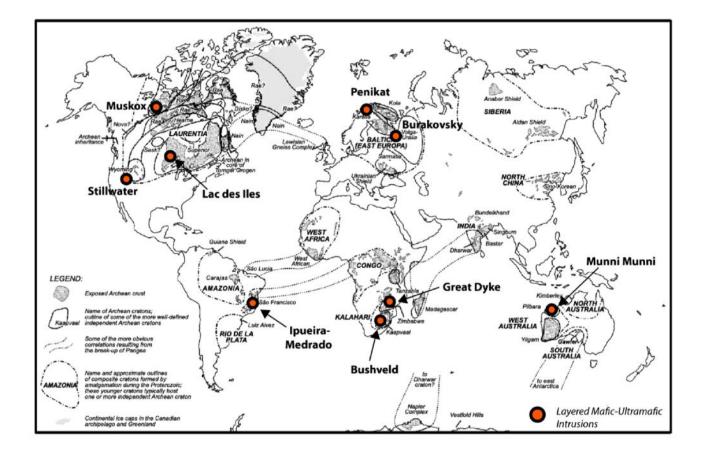
the Sverdlovsk region of Russia's Ural Mountains and is a popular recreation spot – a fact which has sparked conflicts over the mine's development.

South Africa

The **Bushveld Igneous Complex (BIC)** is the largest layered igneous intrusion within the Earth's crust. It is approximately 2 billion years old and is divided into four different limbs: the northern, southern, eastern, and western limbs. The Bushveld Complex comprises the Rustenburg Layered suite, the Lebowa Granites and the Rooiberg Felsics, that are overlain by the Karoo sediments. The site was first discovered around 1897 by Gustaaf Molengraaff. Located in South Africa, the BIC **contains some of the richest ore deposits on Earth**. The Complex includes **layered mafic intrusions** (the Rustenburg Layered Suite) and a felsic phase.

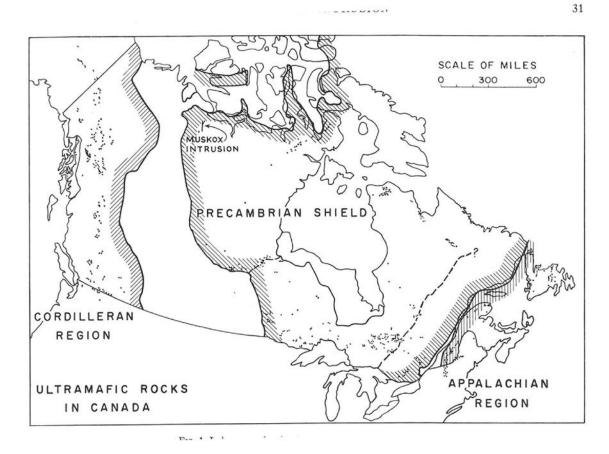
Layered Mafic-Ultramafic Intrusions

Djon (2017) referred to the Lac de Iles deposits as **Layered Mafic-Ultramafic Intrusions** and provided the following map of other similar sites throughout the world.



We will take this as a opportunity to include these regions in this listing. Lac des Iles and Stillwater were covered above.

Muskox Intrusion outcrops are in the north- western corner of the Canadian Shield. The intrusion is a Precambrian layered basic pluton, **74 miles in length**. The central layered series is **8500 feet thick** and contains 38 main layers of dunite, peridotite, pyroxenites and gabbros which vary in thickness from 10 to 1800 feet. The Muskox intrusion has a higher olivine content than would normally be expected (Smith and Kapp, 1963).



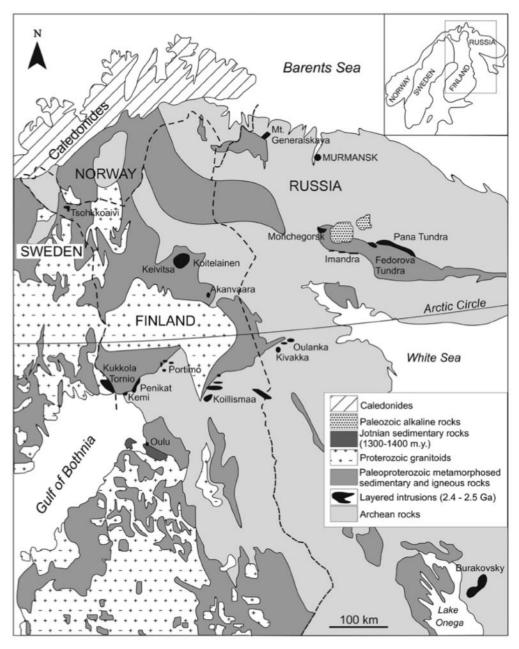
The Muskox Intrusion is in the northwestern corner of the Precambrian Shield

The **Stillwater igneous complex** is one of the world's great layered mafic intrusions, distinguished not so much by its size as by the fact that it is tilted on its side, and **erosion has exposed the layering to ready access**. It is a large layered mafic intrusion located in southern Montana in Stillwater, Sweet Grass and Park Counties. The complex is exposed across **30 miles** of the north flank of the Beartooth Mountain Range. The complex has extensive reserves of chromium ore and has a history of being mined for chromium. More recent mining activity has produced palladium and other platinum group elements. The Basal zone is composed of a variety of rocks, including Cumulates, principally

orthopyroxene cumulates but with minor amounts of one- and two-phase cumulates **dominated by olivine**, orthopyroxene, clinopyroxene, inverted pigeonite, and plagioclase.

The **Penikat** layered ultramafic-mafic intrusion in Northern Finland is one of te most richly mineralized layered intrusions on Earth.

The **Burakovsky layered complex**, consisting of 2,430 Ma, is located in Karelia, Russia, is one of the largest layered Fennoscandian intrusions. It consists, from the base to the top, of a thick ultramafic part **dominated by dunite and peridotite** overlain by a layered mafic part that consists of alternating layers of pyroxenite, wehrlite and gabbro (Transitional Banded Zone, TBZ), and a thick sequence of gabbroic rocks [Gabbronite Zone (GNZ), Pigeonite Gabbronorite Zone (PGNZ), Magnetite Gabbronorite–Diorite zone (MGDZ), which predominates (Bailey et al, 2011).



Schematic geological map showing the location of the main Paleoproterozoic layered intrusions in the Fennoscandian Shield (after Alapieti & Lahtinen 2002).

The **Great Dyke** is a linear geological feature that trends nearly north-south through the centre of Zimbabwe passing just to the west of the capital, Harare. It consists of a band of short, narrow ridges and hills spanning for approximately 340 mi. The range is host to vast ore deposits, including gold, silver, chromium, platinum, nickel and asbestos. The Great Dyke of Zimbabwe is unique within the family of large-layered intrusions by virtue of its highly elongate form.



NASA Image

It is rich in chromite which is enclosed in cumulus olivine high in Fe^{2+} .

The Bushveld Complex is the world's largest layered intrusion, and because of its unique character most other layered intrusions are compared with it. The Bushveld Complex, as exposed at current levels of erosion, consists of eastern, western and northern limbs, and is some seven to nine kilometres thick. Despite its size the amount of olivine is limited.

The **Munni Complex** is a layered sequence of clinopyroxenite, peridotite, and gabbro within the Archean Pilbara Block, Western Australia. The intrusion has been tilted, exposing some 2000 m of layered ultramafic rocks overlain by over 3500 m of gabbroic rocks.

Ophiolite Sites around the World from Wikipedia

North American Cordillera (a system or group of parallel mountain ranges together with the intervening plateaus and other features, especially in the Andes or the Rockies). Coast Range Ophiolite, in the California.

Exposures straddle the coast from Santa Barbara County up to San Francisco. The formation then trends inland up to the southern end of the Klamath Mountains.[1a]

Coast Ranges from Santa Barbara through San Francisco Counties, California.

Kings River ophiolite, southwest Sierra Nevada foothills.

California Point Sal ophiolite, Point Sal, Santa Barbara County, Southern California. California ophiolite-Smartville Block of the Sierra Nevada, and the Klamath Mountains. Northern California Josephine Ophiolite. Southern Oregon Canyon Mountain. Sparta Complexes ophiolite, Northeastern Oregon. Payson Ophiolite, Payson, Arizona. Metchosin Igneous Complex ophiolite, southern Vancouver Island, British Columbia, Canada. Ingalls Terrane ophiolite, Cascade Mountains, Washington Fidalgo Complex ophiolite, Skagit County, Washington.

Eastern North America

Betts Cove, St. Anthony,
Little Port Advocate.
Gander River, Pipestone Pond.
Great Bend and Annieopsquotch ophiolites in Newfoundland Bay of Islands.
Ophiolite in Gros Morne National Park, Newfoundland, named a UNESCO World Heritage Site in 1987 because of its superbly exposed complete ophiolite stratigraphic sequence [6]
Thetford Mines ophiolite Complex (Thetford Mines, Cantons de l'Est, Québec, Canada) [7][8].
Asbestos ophiolite (Asbestos, Cantons de l'Est, Québec, Canada) [8]
Mont Orford ophiolite (Magog, Cantons de l'Est, Québec, Canada) [8].
Mont Albert ophiolite (Gaspésie, Québec, Canada) [9]
Maryland ophiolite in the central Appalachian orogen, Baltimore, Maryland. [10]

Mexico and the Caribbean

Olivos ophiolite, Chihuahua, Mexico. Vizcaino ophiolite, Baja California Sur Mexico. Cuban ophiolititic belt Puerto Rican ophiolite

Mediterranean and Peri-Arabic

Morais ophiolite complex, Portugal Internal Ligurian Ophiolites in Northern Apennines, Italy. Troodos Ophiolite in the Troodos Mountains of Cyprus. Kizildag ophiolite, southern Turkey Cap Corse ophiolite, Corsica, France. Vourinos and Pindos Ophiolites in Northern Greece and their northern extensions. Albania, Serbia and Bosnia Ronda peridotite, Southern Spain Lherz Massif, France. Beni Bousera ophiolite, Morocco. Golyamo Kamenyane Complex, Bulgaria [2]. Semail Ophiolite in Oman and the United Arab Emirates. Makran Ophiolite, Makran, Iran. Pakistan Zagros ophiolite, Zagros mountains, Iran. Iraq Zagros ophiolites, Zagros mountains, Iraq, includes; Cretaceous ophiolites (Mawat, Penjwen, Pushtashan, Hassanbig and Bulfat) and Eocene ophiolites (Rayat and Qalander).

Tibetan

Dongbo ophiolite Loubusa ophiolite Purang ophiolite

Asia-Pacific

Zambales Ophiolite in western Luzon, Philippines.

Angat Ophiolite in eastern Luzon, Philippines. Rapu-rapu Ophiolite Complex in eastern Philippines. Southeast Bohol Ophiolite Complex in Bohol, Philippines. Macquarie Island, Tasmania. Australia Palawan Ophiolite. Western Philippines. Papuan ophiolite in Papua New Guinea Yakuno, Horokanai, and Poroshiri. Three full ophiolite sequences in Japan Dun Mountain Ophiolite Belt, South Island, New Zealand Naga-Manipur Ophiolite Complex, India

Andes

La Tetilla Ophiolite Complex, near Popayán. Colombian Cordillera Occidental (Andes) Famatinian Ophiolites, near Famatina in the Argentine Andes. Tapo ophiolite, Peru [2] Taitao ophiolite Rocas Verdes ophiolites, Patagonian Andes, Chile [4] Tortuga ophiolite complex Sarmiento ophiolite complex

Brazil

Quatipuru ophiolite, Brazil. Cerro Mantiqueiras Ophiolite, Rio Grande do Sul, Brazil

Northern Europe

Ballantrae Ophiolite Complex.
Girvan-Ballantrae area, SW Ayrshire, Scotland.
Jormua Ophiolite, Finland [1]
Karmøy ophiolite, Scandinavian Mountains, Norway [12]
Leka Ophiolite, Scandinavian Mountains, Norway [13]
Løkken Ophiolite, Scandinavian Mountains, Norway [13]
Nuttio Ophiolite, Finland [1]
Solund-Stavfjord Ophiolite, Scandinavian Mountains, Norway.
Lizard complex in Cornwall, United Kingdom [14].
Outokumpu Ophiolite, Finland [1]
Shetland Ophiolite, Unst and Fetlar, Shetland, Scotland [15]

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For Appendices E to H Go to www.thecomingsfoundation.org

Some Final Thoughts

The internet is replete with YouTube videos of Direct Air Capture companies marveling about how effective their technologies are for capturing thousands of tons of CO₂ and eventually reaching megatons and then gigatons. However, they present very little discussion of the 10 problems listed on pages 23 to 26 of this document.

There was no discussion of the Jahediesfanjani, et al (2018) assessment that many of the potential underground storage sites in the U.S. already contain a large amount of carbon in various forms, and when these containing over 50 percent of such carbon are excluded, there is barely room for a third of a gigaton of underground storage, far less than the 1,000 plus gigatons of storage needed by the end of the century.

There was no discussion of the Bartholomew and Mauter (2021) concern that many of the basalt domes are filled with saline three times more concentrated than seawater, and the expense involved for removing that.

And there was especially no discussion of the almost certain danger that one or more of the required 1,200,000+ one megaton burials of CO₂ gas will leak causing a Lake Nyos type of event with devastating consequences.

<u>There is far more room on the surface of the earth and in the ocean, to store CO_2 in mineralized form, than there is underground to safely store CO_2 gas. I laud the fine progress these DACS companies have made, but they cannot do the job alone.</u>

We did not win World War II until we opened a second front. <u>We will not win the war</u> <u>against global warming unless the U.S. Government and DOE open a second front in the</u> <u>form of initiating these four additional NETs - EW, OAE, eOAE and heOAE.</u>

The Military (DOD) has stated that the war against climate change is just as vital to win as any shooting war we might be involved in. Post WWII shooting wars involved significant local disruptions, while the rest of the world is only marginally affected. By contrast, the war on global warming involves every country on the planet and if we lose it, there will be no livable planet left.

While this review concluded that EW, OAE, eOAE and heOAE are capable of safely sequestering gigatons of CO₂/year, there are many other NETs that can also sequester CO₂, but at a lesser level of sequestration. These have been reviewed elsewhere (NAS 2019, 2021; EFI 2019, 2020a; Kormor 2022; Cobo et al, 2023; and others). Many of these should also be part of the Carbon Dioxide Removal picture so that DACS, EW, OAE, eOAE and heOAE are not required to carry the whole load.

The removal and sequestration of over a thousand gigatons of atmospheric CO_2 by the end of the century **will be a huge undertaking**. Currently it is largely in the hands of a few companies requiring multi-million-dollar machinery and large grants and involving the potentially dangerous burial of gigatons of CO_2 underground. There are serious concerns that this will work. What is needed is the **democratization of CDR**.

As discussed above, one of the potentially most powerful aspects of EW and heOAE is the possibility that the drone program and the catamaran program would allow many thousands of youthful climate activists worldwide to actively patriciate in the process of safely removing CO_2 from the atmosphere. This could be facilitated by the development of a CDR Corp analogous to the Peace Corp. This could best be run by the U.S. government and would train some of the thousands to climate change activists, especially our youth who have the most to lose. This would involve the training in the use of drones to spread ground climate rocks on croplands and non-croplands throughout the world for the sequestration of CO_2 on land, and training in the use of many hundreds of heOAE catamarans for the removal and sequestration of CO_2 from the ocean and combating ocean acidification.

The potential of heOAE is particularly exciting.

- It is capable of safely sequestering gigatons of CO₂.
- It does not require the expense of pulling CO₂ out of the air.
- It avoids the potentially dangerous practice of burying gigatons of CO₂ underground.
- It does not require mining, processing, and distributing gigatons of climate rocks.
- It also combats ocean acidification (which DACS does not do)
- It avoids the risk of putting heavy metals in the ocean.
- It avoids the many problems with geoengineering (Fox, 2023).
- It can be placed on sail driven catamarans allowing them to go throughout the ocean on wind power alone.
- This would allow them to focus on areas of greatest need such as the Great Coral Reef and areas of CO₂ outgassing.
- The electricity required can be provided by a series of shore and mid-ocean solar and/or wind turbine islands.
- Each catamaran outfitted with heOAE technology would cost about \$1.5 million.
- \$1.5 billion could build a thousand of them.
- World-wide there are over 400 non-profits devoted to climate change with thousands to millions of activist members, especially young people who have the most to lose if global warming continues unabated. This would allow democratizing of the process of CO₂ removal instead of leaving it to a few companies needing multimillion dollar equipment and billions in grants.
- Once the ships and solar or wind turbine islands are paid for, since only renewable electricity is required, it would allow for the continued sequestration of CO₂ for many years, at a very low cost, saving billions of dollars.
- Depending on foundation funding, we propose to research all aspects of heOAE, i.e.
 - What is the best second half of the hybrid electrolysis technique? What are the best batteries?
 - What are the best fuel cells?
 - What is the best design for the ship?
 - What is the best source of electricity?
 - What are the best sizes for the electrolysis, fuel cells, batteries and

catamarans? How many tons of CO₂ could such a ship sequester each year? And many others.

As outlined in the *Addendum* we would also encourage the different existing branches of the government to answer these questions and build a prototype research vessel.

The world temperatures are steadily rising with increasingly severe consequences. We need Manhattan and Apollo Program type involvement and similar deadlines to solve the climate crisis. <u>The time to do so is NOW</u>.

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- Review of the potential problems of Direct Air Capture and Storage (DACS)
- Description of the use of EW, OAE, eOAE and heOAE to sequester mineralized CO₂ above ground or in the ocean and is far safer than burying gigatons of CO₂ gas.
- Description of Tropical Weathering Hot Spots and Artificial Weathering Hot Spots.
- Use of the term climate rocks for ultramafic and mafic rocks.
- Developing U.S. Navy Nuclear powered heOAE ships.
- Proposal to use mid-ocean floating solar and/or wind turbine islands to power heOAE.
- Proposal to use OTEC to power heOAE.
- Combating Ocean Acidification, Deoxygenation and Warming
- Rescuing the Barrier Reef Corals
- OAE/eOAE/heOAE targeted to regions of CO₂ outgassing
- Decreasing NO₂ and CO₂ Emissions on Land and the Ocean
- Encourage the U.S. Navy and NOAA to develop an OAE/eOAE/heOAE Corps
- Exploration of the use of vertical "farming" to accelerate EW
- Encourage the Government to develop Mining and Grinding of Climate Rocks at Twin Sisters, WA, and elsewhere in the U.S.
- Encourage the *in-situ* and *ex-situ* use of climate rocks in New Caledonia
- Encourage the US/UN to set up a Global EW/OAE/eOAE/heOAE Organization
- Have the governments of the world or philanthropists pay for a fleet of catamarans carrying HeOAE technology to combat ocean acidification.
- Plans for how individuals in Climate Change Non-profits, NGOs, billionaires, and wealthy philanthropists can actively participate in sequestering atmospheric CO₂

We urge the US/UN to Initiate an International Plan of having all Nations Commit to both Reducing Emissions AND using EW, OAE, eOAE and heOAE to sequester CO₂ as powerful and safe adjuncts to DACS

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