

## Putting Mafic Rocks in the Ocean

An alternative to spreading mafic rocks on cropland is spreading them into the ocean. The above maps on the location of mafic rocks in the US shows that some of the highest concentrations are close to the Pacific coast. By contrast, there are fewer sites in the Midwest where most of the farming is. This raises the question of whether it would be more efficient to dump finely ground mafic rocks directly into the ocean. This possibility is examined below.

## Scientific Studies of Olivine Weathering

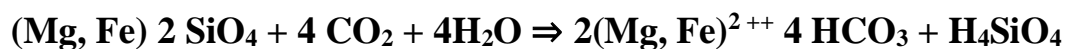
### A. Weathering of Olivine in Soil

There have been more experimental investigations of the reactivity of olivine than any other multi-oxide silicate mineral. For example, Oelkers et al (2018) review cites over 70 references. In contrast with most other minerals, olivine reactivities measured in different studies and using distinct experimental methods tend to be consistent with one another. Some of these studies will be reviewed here.

**Wogelius and Walther (1992)** In one of the early studies these authors found that the dissolution rate at a given pH at 25°C, for iron rich fayalite olivine (Fe<sub>2</sub>SiO<sub>4</sub>) was 6 times faster than magnesium rich forsterite olivine (Mg<sub>2</sub>SiO<sub>4</sub>). Clearly the type of olivine is an important factor. However, magnesium olivine is more common and most of the following studies were performed with the magnesium rich olivine.

**Schuiling and Krijgsman (2006)** The title of this article is: *Enhanced Weathering: An Effective and Cheap Tool to Sequester CO<sub>2</sub>*. The question is, do 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 CO<sub>2</sub>-levels in the atmosphere down.

Olivine (Mg<sub>2</sub>SiO<sub>4</sub>) is an abundantly available magnesium silicate which weathers according to the reaction



This formula indicates that **4 mol of CO<sub>2</sub> are sequestered by 1 mol of olivine**, equivalent to **1.25 t of CO<sub>2</sub> (or 0.34 t of C) per ton of olivine**.

Olivine is a cheap and widely available material. By the authors' calculations, in order to neutralize the CO<sub>2</sub> 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 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 CO<sub>2</sub>.

As to the nickel in olivine the authors state 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 no 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 bio-available.**

In conclusion, they state that point sources of CO<sub>2</sub> 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 CO<sub>2</sub>, 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.

**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 1630 (OLIV1), 8150, 40,700 and 204,000 (OLIV4) 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 estimated from a Mg balance was equivalent to 240 kg/ha (14.8% of dose, OLIV1) to 2240 kg/ha (1.1%, OLIV4). **This corresponds to gross CO<sub>2</sub> sequestration of**

**290 to 2690 kg/ha** similarity with kieserite treatments ranged from 13% to 58% for OLIV1. Weathering appears fast enough to support the ‘enhanced weathering’ concept. In agriculture, olivine doses must remain within limits to avoid imbalances in plant nutrition, notably at low Ca availability; and to avoid Ni accumulation in soil and crop.

**Note how much more understandable the Berge et al statement that the rate of weathering corresponds to gross CO<sub>2</sub> sequestration of 290 to 2690 kg/ha versus the Renforth et al statement that the rate of weathering was between 10<sup>-16.4</sup> and 10<sup>-15.5</sup> moles(Mg)/cm<sup>2</sup>/s.** Although the latter is based on the math of the Olsen model that does not make it clear to the average reader. Why use seconds instead of days or months? Why weird exponentials like 10<sup>-16.4</sup> instead of a more understandable 2 x 10<sup>-16</sup>?

**Renforth, (2012)** The silicate resources in the UK are large and could theoretically capture 430 billion tons (Gt) of CO<sub>2</sub>. The majority of this resource is contained in basic rocks (with a carbon capture potential of ~0.3 tCO<sub>2</sub>/t rock). There are a limited number of ultrabasic formations (0.8 tCO<sub>2</sub>/t rock) with a total carbon capture potential of 25.4 GtCO<sub>2</sub>. It is shown that the energy costs of enhanced weathering may be 656–3501 kWh/tCO<sub>2</sub> for basic rocks and 224–748 kWh/tCO<sub>2</sub> for ultrabasic rocks. Comminution and material transport are the most energy intensive processes accounting for 77–94% of the energy requirements collectively. The operational costs of enhanced weathering could be £44–361/tCO<sub>2</sub> (\$70–578/tCO<sub>2</sub>) and £15–77/tCO<sub>2</sub> (\$24–123/tCO<sub>2</sub>) 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.

**Moosdorf, N. et al (2014)** Terrestrial enhanced weathering consumes more CO<sub>2</sub> than it emits for mining, comminution, transport, and application in most locations. The CO<sub>2</sub>-efficiency is dominated by the choice of source rocks and material comminution. CO<sub>2</sub> emissions from transport have a small effect on the overall budget (on average 0.5-3% of potentially sequestered CO<sub>2</sub> and the emissions of material mining and application are negligible. After all emissions, 0.5-1.0 t CO<sub>2</sub> 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 CO<sub>2</sub> 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.

**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.** On the basis of 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)/cm<sup>2</sup>/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.

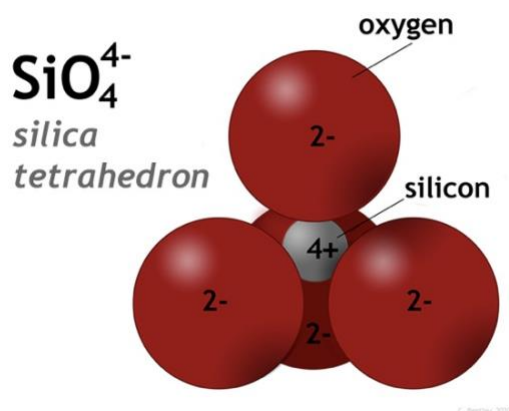
A number of workers have suggested that the release of potentially toxic elements during the dissolution of olivine may pose an environmental risk which would subsequently lower the potential of terrestrial enhanced weathering (Hartmann et al., 2013; Renforth, 2012). From the results of this study, there was elevated Cr in 5 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.**

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  $\mu\text{m}$  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  $\text{CO}_2$  uptake such as direct air capture).

**Oelkers et al. (2018)** Olivine dissolution reactivity is relatively simple. Its structure is comprised of isolated  $\text{Si-O}^4$  4-tetrahedra linked by divalent cations.



Aqueous species that adsorb to these bonds apparently accelerate their destruction. For example, the absorption of  $\text{H}^+$ ,  $\text{H}_2\text{O}$  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 1) pH, 2) water activity, 3) temperature, and 4) mineral-fluid interfacial 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. Each of these factors

limits and or influences the application of forsterite dissolution to 1) enhanced weathering efforts, 2) mineral carbonation, and 3) the low temperature generation of hydrogen or hydrocarbons via the oxidation of its divalent iron.

Olivine dissolution can **proceed by the breaking of just the ionic Mg-O bonds, liberating the  $\text{SiO}_4^{4-}$  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.**

**Philip A.E. 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  $\text{CO}_2$  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.

### **B. Weathering of Olivine in Oceans (Seawater)**

**Kheshgi, (1995).** Ocean alkalinity might be raised by introducing the dissolution products of alkaline minerals into the oceans. **Naturally occurring soda ash ( $\text{Na}_2\text{CO}_3$ ) 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  $\text{CO}_2$ , 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  $\text{CO}_2$  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

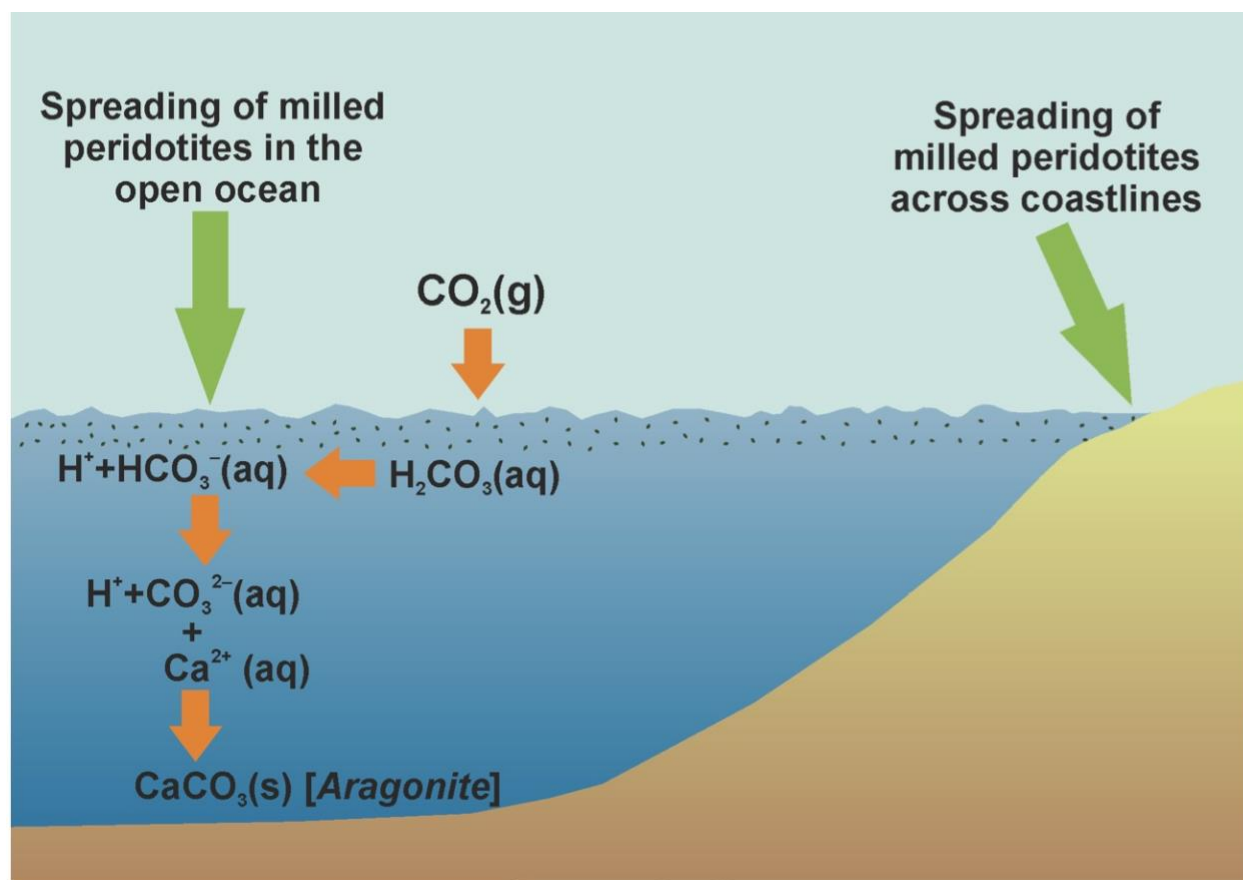
materials that can be safely and permanently kept out of the active carbon stocks in the environment. Carbonate sequestration methods require the development of an extractive minerals industry that provides the base ions for neutralizing carbonic acid.

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  $PCO_2$  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  $PCO_2$ ,  $[CO_3^{2-}]$  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  $PCO_2$ .

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. If we concluded that increasing the alkalinity of the ocean in the area of the Great Barrier Reef would help to save the reef, we would **need to bring Lackner on as a consultant.**

**Rigopoulos et al (2017)** The following figure is from Rigopoulos et al: Carbon sequestration via enhanced weathering of peridotites and basalts in seawater (2017).



This study was designed to assess the potential drawdown of CO<sub>2</sub> 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 mafic and 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 CO<sub>2</sub> 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<sub>2</sub> 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.

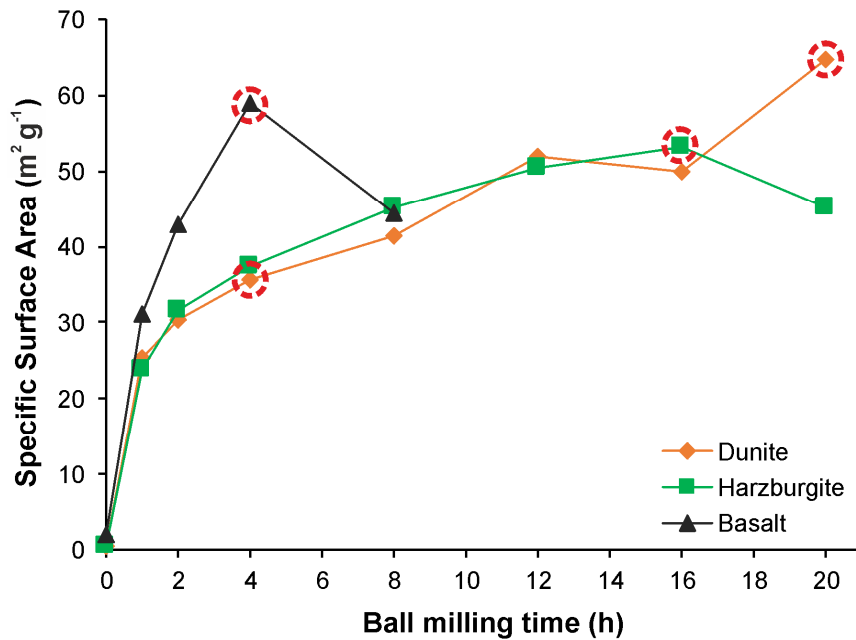
### What is ball-milling?



A ball mill 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.

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.

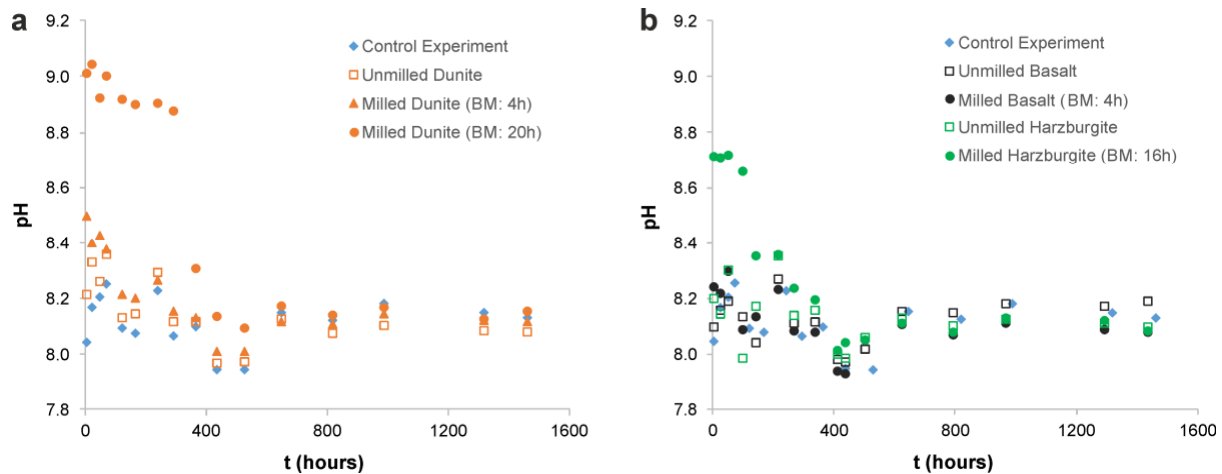
The effect of various times in the ball-mill was measured by the BET method (adsorption of N<sub>2</sub> at 77 K) and was carried out in a Micromeritics Gemini III Surface Area and Pore size Analyzer in order to determine the specific surface area (m<sup>2</sup>/g).



BET ( $\text{m}^2/\text{g}$ ) 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).



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.** This is relevant to the relative effect of these three milled minerals in combating ocean acidification.

The conclusions of this study were:

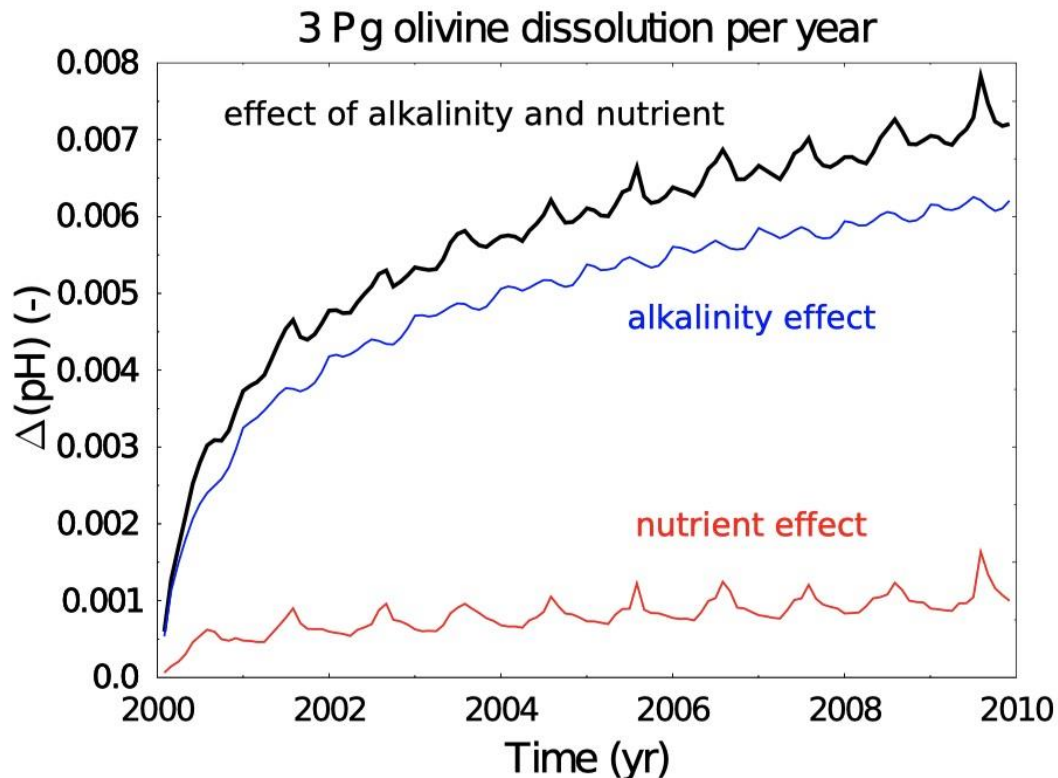
- Peridotites induced CO<sub>2</sub> drawdown directly from the atmosphere via mineralization.
- The basalt did not yield any significant changes in seawater composition.
- The precipitation of sepiolite could reduce the carbon sequestration efficiency.

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<sub>4</sub>Si<sub>6</sub>O<sub>15</sub>(OH)<sub>2</sub>·6H<sub>2</sub>O, it can be present in fibrous, fine-particulate, and solid forms. Only small amounts of it were formed in the grinding process.

**Kohler et al (2013)** 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 μm 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.



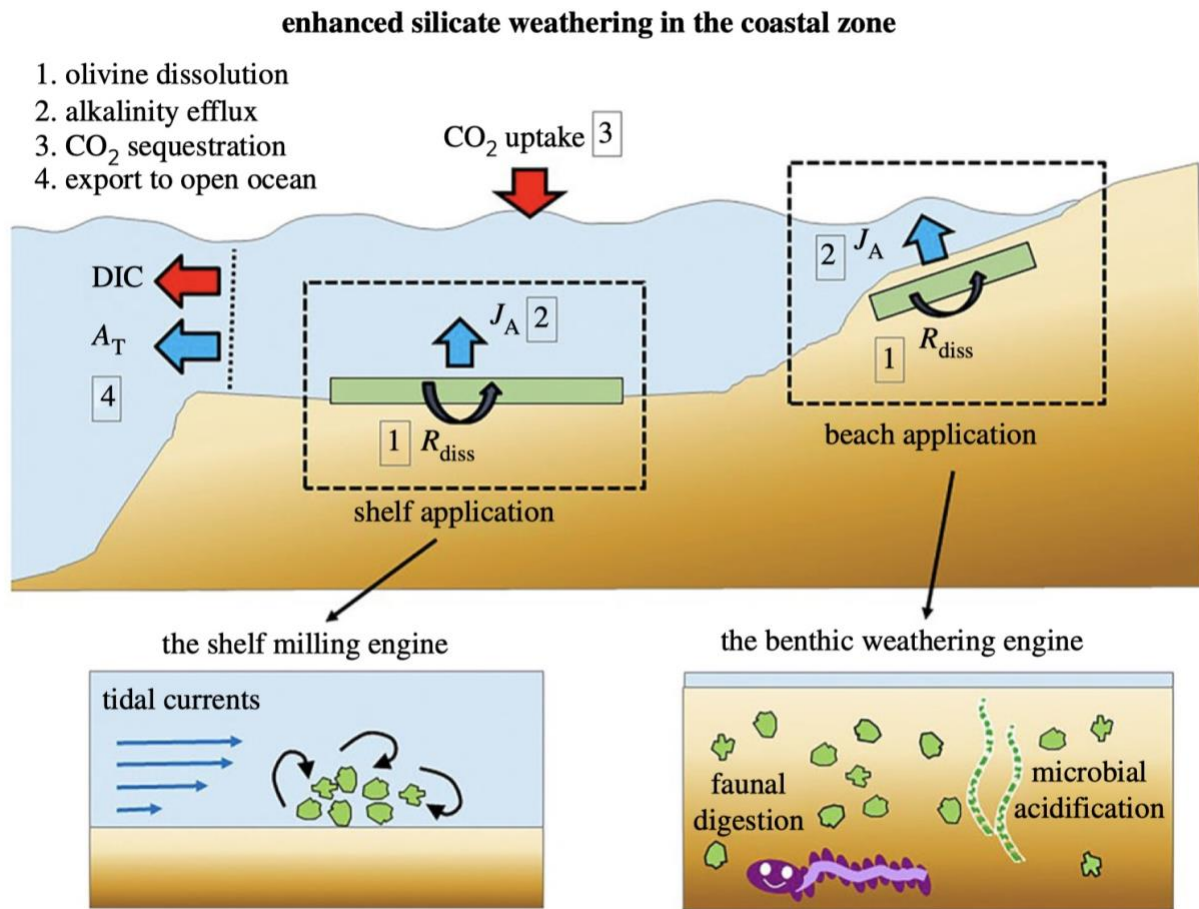
The placement of large amounts of olivine into the ocean is not without potential problems, listed as follows. Its **limitations** are: distributing 3 Pg olivine per year: **full-time commitment of more than 300 large ships**. This would sequester approx. 9% of anthropogenic CO<sub>2</sub> emissions.

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.

**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<sub>2</sub> may be released to the atmosphere and ocean pH might decrease during oxic olivine weathering. Ocean alkalization only happens when more than 1 mol/kg H<sub>2</sub>O 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 as holds 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.

**Meysman FJR and Montserrat F. (2017)** These authors discuss the potential of applying ESW 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 CO<sub>2</sub> sink. Compared with other NETs, coastal ESW 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 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

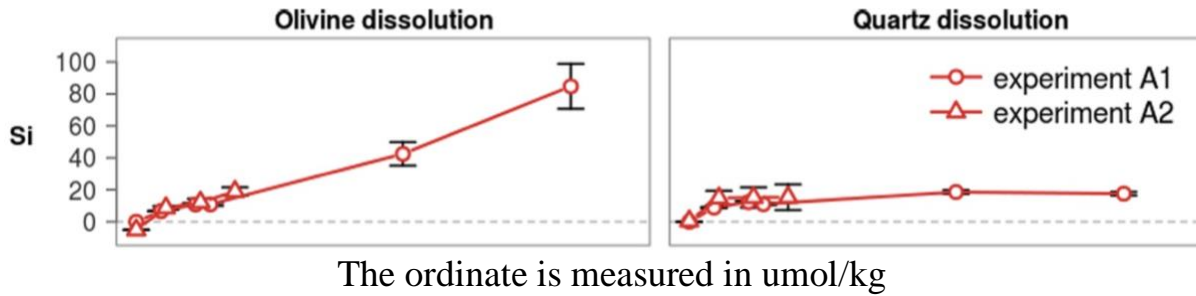
beaches and shallows, where dissolution is enhanced through biotic processes in the seabed ('benthic weathering engine').

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. The authors propose the concept of the 'benthic weathering engine', 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 more precisely determine the weathering rate 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)** The authors specifically address a number of questions related to the application of enhanced silicate weathering 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<sub>2</sub> sequestration efficiency of olivine dissolution in seawater?

Commercially available olivine sand ( $\text{Mg}^{2-x}\text{Fe}^x \text{SiO}_4$ ) and lab-grade quartz ( $\text{SiO}_2$ ) were used in slurry dissolution experiments. The olivine sand (particle size quantiles: D10 = 91  $\mu\text{m}$ , D50 = 143  $\mu\text{m}$ , D90 = 224  $\mu\text{m}$ ) had a molar Mg-to-Fe ratio of 0.94:0.06, characterizing the olivine as forsterite-94 ( $\text{Fo}_{94}$ ). 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 main consequences of forsterite olivine dissolution are increases in  $Mg^{2+}$ , Si, TA (total alkalinity), DIC (dissolved inorganic carbon),  $Fe^{+2}$ , and  $Ni^{+2}$ , and their ecosystem effects should be thoroughly 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  $CO_2$  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.

**Nickel Issues** The impact of increased nickel flux on marine ecosystems is a matter of potential concern. Ecosystems 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  $0.25 \mu\text{mol/L}$ . Nickel toxicity has been reported in a number of cases: negative effects on spawning in mysiid shrimps at  $2.4 \mu\text{mol/L}$ , DNA damage with associated physiological and cytotoxic effects in the blue mussel *Mytilus edulis* at  $0.3 \mu\text{mol/L}$ , disrupting ionoregulatory functions in the green crab *Carcinus maenas* between  $8.5$  and  $51 \mu\text{mol/L}$  in very low-salinity seawater ( $0.006$  PSU), and organ oxidative stress in the killifish *Fundulus heteroclitus*.

The potential toxicity of nickel, combined with rather large uncertainties about the magnitude and direction of its response effects, make it paramount to further investigate its ecotoxicological effects within the framework of large-scale application of olivine in coastal environments.

Before beginning any field-scale application, there should be proper field trials in quasi-contained conditions, such as mesocosm setups, which can be upscaled in, e.g., tidal harbor basins. In the case that a mesoscale field trial ( $\sim 100 \text{m}^2$ ) would be undertaken, common dredging equipment would be used to apply the olivine into the (coastal) environment. The same equipment and expertise can be used to remove the olivine sand, should any acute unforeseen situation develop.

The CO<sub>2</sub> sequestration induced by ESW is governed by the acid–base thermodynamics of seawater, which are well understood, therefore rendering the containment of CO<sub>2</sub> in the ocean highly predictable. The central premise of ESW is that it increases the ocean’s alkalinity, enabling more CO<sub>2</sub> to be dissolved into seawater at any given pCO<sub>2</sub> compared to the situation in which no alkalinity is added to the ocean.

If ESW is ever to be applied in a geo-engineering framework, it is of paramount importance to investigate the effects of all of these natural processes on the dissolution of olivine in coastal environments.

**Hangx and Spiers (2009)** The feasibility of spreading olivine on coast lines depends on the rate of olivine dissolution, the sequestration capacity of the dominant reaction, and its CO<sub>2</sub> footprint. Kinetics calculations show that offsetting 30% of worldwide 1990 CO<sub>2</sub> emissions by beach weathering means distributing of 5.0 Gt of olivine per year. For mean seawater temperatures. To obtain useful, steady state CO<sub>2</sub> 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<sub>2</sub> 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 CO<sub>2</sub> 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.

**They concluded that coastal spreading of olivine is not a viable method of CO<sub>2</sub> sequestration on the scale needed.** The method certainly cannot replace CCS technologies as a means of controlling atmospheric CO<sub>2</sub> concentrations.



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.

It is surprising that the grinding of olivine would only decrease efficiency by 5 to 20%. This seems doable.