

# ENHANCED WEATHERING: AN EFFECTIVE AND CHEAP TOOL TO SEQUESTER CO<sub>2</sub>

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**Abstract.** Weathering and subsequent precipitation of Ca- and Mg-carbonates are the main processes that control the CO<sub>2</sub>-concentration in the atmosphere. It seems logical, therefore, to use enhanced weathering as a tool to reduce rising CO<sub>2</sub>-levels. This can be applied as a technology, by reacting captured CO<sub>2</sub> with olivine or calcium-silicates in autoclaves. It can also be applied extensively, by spreading fine-powdered olivine on farmland or forestland. Measures to control the CO<sub>2</sub>-levels of the atmosphere will be adopted more readily if they also serve some broader economic goals. An effective strategy for CO<sub>2</sub> control will require many parallel approaches simultaneously.

## 1. Introduction

The fact that Venus has a dense CO<sub>2</sub>-atmosphere, whereas CO<sub>2</sub> is only a minor constituent of the Earth's atmosphere is due to the fact that on Earth running water (occasionally also wind or ice) is continuously removing weathered rock and exposing fresh rock, whereas on Venus such a continued renewal is absent. The earth is thought to have a similar CO<sub>2</sub> inventory as Venus, but instead of the bulk of it being in gaseous form, most of it exists as carbonate rocks: the product of the chemical weathering of silicates under aqueous conditions. Holland (1984) summarizes as follows "During most, if not all, of Earth history, CO<sub>2</sub> seems to have been the major weathering agent. Its neutralization has required the conversion of nearly all of the CaO and a part of the MgO in silicate rocks exposed to weathering into limestones and dolomites". Not only the absence of liquid water as a physical agent, but also as an essential chemical agent during weathering has brought interactions between rocks and atmosphere on Venus to a halt.

This has resulted in a build-up of CO<sub>2</sub> in the atmosphere of Venus, which has about a 200,000 times higher concentration than found on Earth. Weathering of fresh rock depletes the earth atmosphere of CO<sub>2</sub>, because chemical weathering can be described by the general equation



The calcium and magnesium released during weathering combine in the oceans with the carbonate to form limestones and dolomites, which are the major sink for CO<sub>2</sub>. The second major sink is organic matter in sediments, hydrocarbons and natural gas that are directly or indirectly the result of photosynthesis.

If there is no supply of fresh rock or liquid water close to the surface of the planet, the formation of carbonates or organic carbon stops.

## 2. Sequestration of CO<sub>2</sub>

The recent build-up of the concentration of CO<sub>2</sub> brought about by the rapid combustion of fossil fuels is a cause of concern, and attempts are being made to store CO<sub>2</sub> in reservoirs other than the atmosphere. Among these we can mention biomass (all living organic matter, like forest on land, and plankton in the oceans), and disposal in deserted gas fields or aquifers, or in the deep ocean.

The use of some of these sinks may have additional benefits, such as wood production on land, increased fish production at sea, improved soil quality by increased storage of soil organic carbon (Swift, 2001), buffering of acid rain or acid soils by olivine, enhanced methane recovery by injection of CO<sub>2</sub> in coal beds and enhanced recovery of oil and gas by using CO<sub>2</sub> as a propellant and a means to reduce the viscosity of the oil.

In the following we will examine the option of enhanced weathering and its potential economic benefits.

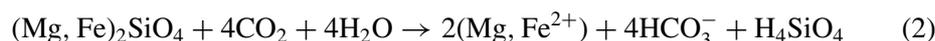
*Weathering, until recently, has received little attention, although it is the most important way in which nature keeps the CO<sub>2</sub>-levels in the atmosphere down.*

This oversight is probably due to the fact that people are unaware of its potential for CO<sub>2</sub>-sequestration, or don't see a practical way to accelerate weathering.

Minerals and volcanic glasses display very different rates of weathering. Among the major silicates, olivine weathers fastest, whereas quartz hardly weathers at all. In addition, of course, weathering rates are not only a function of rock-type but also of temperature, rainfall and accessibility of the rock. Crushed olivine in a wet and not too cold climate will weather rather fast. Even so, however, weathering proceeds slowly from the perspective of a technological process. From the experimentally determined rate of weathering it can be calculated that an addition of 1 to 2 tons of crushed olivine (grain size <300 micron) to one ha of soil will last approximately 30 years in a temperate climate. The calculation is as follows. Assumed rainfall 75 cm/yr, pH 4, so each liter of rainwater contains 10<sup>-4</sup> g of H<sup>+</sup>. In 30 years every square meter receives  $30 \times 7.5 \times 100 \text{ dm}^3 \times 10^{-4} \text{ g H}^+/\text{dm}^3 = 2.25 \text{ g H}^+$ . To neutralize this with olivine, according to reaction (2)  $2.25/4 \times 140 \text{ g}$  olivine is needed, equivalent to 80 g olivine/m<sup>2</sup>, or 800 kg/ha. For every drop or rise of the pH of the rain by 0.3 units, the amount of olivine to be applied must be doubled, respectively halved. If the pH of the rainwater is 5, weathering of the same amount of olivine will take 300 years.

Just for the sake of argument, let us calculate how much olivine we would need theoretically to remove all the CO<sub>2</sub> currently in the atmosphere. Evidently, this reaction would never go to completion, because it would slow down the more the CO<sub>2</sub> becomes depleted. The atmosphere exerts a pressure of 10 tons per square

meter, of which 1 part in 2000, or 5 kg per square meter is provided by CO<sub>2</sub>. In order to neutralize 5 kg of CO<sub>2</sub> according to Equation (2) we need to spread a layer of olivine over the whole surface of 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 (Hooke, 2000), but even much smaller amounts of olivine could sequester already substantial amounts of CO<sub>2</sub>.

It should be clear that the above calculation does not represent a realistic approach. Most of the land surface is unavailable for dunite application, or the local rainwaters or soils are not acid. The method is effective in areas with acid rain, or acid sulfate soils. Neutralization is commonly done by liming. Acid rain occurs in large parts of Europe, as well as some parts of Canada and the USA. Acid sulfate soils are common in the Mekong delta or in low-lying areas along the coast of eastern Australia. If the greenhouse problem is going to be tackled, it will probably require a multi-pronged strategy.

### 3. Enhanced Weathering

#### 3.1. ENHANCED WEATHERING AS A TECHNOLOGY

A recent development may bring enhanced weathering within reach. In 1986 we have developed a process by which industrial waste acids are neutralized by reaction with olivine (Schuiling et al., 1986). The process and its products were described in more detail by Jonckbloedt (1997) and Liefink (1997). In direct analogy to this process it was found that under the right conditions ground olivine reacts with compressed CO<sub>2</sub> in autoclaves in a matter of hours, in the presence of a suitable catalyst. A similar approach was recently proposed by Goldberg et al. (2001). The sequestration of fossil carbon as carbonates is reviewed by Lackner et al., 1997. If one starts with olivine, the products are magnesium-carbonate, amorphous silica and an iron-oxide, all environmentally friendly materials with a commercial value. The cost of the technology is estimated by Lackner et al., to be on the order of \$15/t of CO<sub>2</sub>. It is stated that “the cost of the process compares favorably with that of competing approaches”. In this way large amounts of CO<sub>2</sub> can be fixed. If concentrated sources of CO<sub>2</sub> can be captured at their point of origin (refineries, power stations), then this technology should be capable of preventing the CO<sub>2</sub> from reaching the atmosphere. It should be realized that such a process will only be attractive from an economical point of view if the products can be used, e.g. in the building industry.

### 3.2. ENHANCED WEATHERING AS A GEOCHEMICAL ENGINEERING CONCEPT

Although the reaction with olivine seems to be a promising technology to process point sources of CO<sub>2</sub>, it is also worthwhile to investigate the effects of a diffuse application of olivine. This is an example of geochemical engineering (Schuiling, 1990), where a natural geochemical process and/or natural rocks and minerals are used to obtain the desired result. Although acid rain is no longer a big issue in Western countries, thanks to the widespread introduction of desulfurization of stack gases, it is still prominent in many countries, particularly those that depend on lignite combustion for their power production (e.g. Czechia, Slovakia, Poland). Forests in these countries are often in a poor state of health due to the effects of acid rain. If these forest soils could be made less acid by spreading a thin layer of crushed olivine, this would not only help to make the forests healthier, but it would fix CO<sub>2</sub> as well. One could object that the olivine will probably neutralize the stronger acids first, but these have to be neutralized first anyhow, either here or somewhere downstream before the groundwater or surface waters can dissolve sufficient bicarbonate. In agriculture, poor sandy soils are often limed, an action that must be repeated every few years, and that in the light of the greenhouse effect is essentially CO<sub>2</sub>-neutral, as can be seen from reaction (3).



The spreading of lime poses no technical problem on open agricultural land, but is impossible to carry out in standing forests. It is better, therefore, before a new forest is planted, to apply a dose of 1–2 tons of ground olivine per ha which will serve as a pH-buffer against acid rain with a pH of 3.5–4 until the forest is mature, and which will contribute to the fixation of CO<sub>2</sub> from the atmosphere. Acid sulfate soils can also be treated with ground dunite (a rock type that contains more than 90% olivine) to increase their pH.

Weathering can be considered as the neutralization of acids by minerals, and weathering, therefore, adds to the total alkalinity of the earth's waters and soils.

### 3.3. ENVIRONMENTAL CONSEQUENCES OF OLIVINE APPLICATION

Dunites and peridotites contain some nickel. The large Orhaneli dunite complex, for example, contains 0.18% NiO on average (Orgun et al., 2004), equivalent of 0.14% Ni. 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 dunites is chromium, but most of it is tightly bound in very insoluble chromite grains and will not be bio-available.

Asbestos is sometimes associated with ultramafic rocks. Most of the dunites that are currently exploited contain no asbestos, or only small amounts of the non-carcinogenic chrysotile variety (Churg, 1993). When small amounts of chrysotile are admixed in a soil, they will weather similarly to olivine.

One should avoid, of course, to use those rare ultramafic rocks that act as host rocks to ores containing heavy metals like mercury.

#### 3.4. COST CONSIDERATIONS FOR OLIVINE APPLICATION

Olivine is a cheap and widely available material, as it is a major constituent of dunites and peridotites. These are the rocks that make up the Earth's mantle, but that are also found in large massifs at the Earth's surface where they have been pushed up in the course of mountain-building processes. Dunites are mined in a number of countries, and crushed dunite from Spain, for example, costs in the order of a few tens of US\$ per ton in the Rotterdam harbor. Huge olivine reserves in Europe occur e.g. in Norway, Sweden, Spain, Italy, Austria, Greece, Cyprus and Turkey. If we consider Mg-bicarbonate in solution as our end-product, one ton of olivine will sequester somewhat more than 1 ton of CO<sub>2</sub>, which would make this a rather expensive route for CO<sub>2</sub> sequestration. We can, however, subtract the costs of liming, which is only marginally cheaper than the spreading of ground dunite. To achieve an equivalent neutralization, one requires 2 ton of crushed limestone for every 1.4 ton of olivine. Because in most locations the cost of crushed dunite and crushed limestone will be comparable, this means, certainly if one takes into account that the number of applications can be reduced, that the application of dunite instead of liming is cost-effective, even without taking into account the premium of CO<sub>2</sub> sequestration for any area where dunite is within reasonable reach. Even so, in case the transport costs of dunite would be prohibitive in a certain region, it can be replaced by crushed basalt. Worldwide, the largest olivine mines are in Norway. If the fines from olivine mining, which may be even cheaper, can be mixed in the right proportion with a slow-release fertilizer like struvite, preferably in its K-form (KMgPO<sub>4</sub>·6H<sub>2</sub>O, Schuiling and Andrade, 1999), their application to farmland or future woodland should present no problem. In this way we can combine olivine application and the addition of fertilizer in a single activity, providing a buffer as well as a nutrient supply of long duration. In areas where periodic liming is necessary for healthy crops or forests, the application of olivine is cost-effective, because the number of applications can be reduced relative to liming. If the gain in alkalinity in one place can be related to CO<sub>2</sub> sequestration "anywhere" in the Earth system, it should be made possible to collect a premium for the removal of CO<sub>2</sub> under the provisions of the Kyoto protocol. It will probably be necessary, however,

to prove the extent of CO<sub>2</sub> fixation by monitoring the change in composition of the local ground waters after the application of olivine.

#### 4. Conclusions

- Weathering and subsequent precipitation of calcium- and magnesium-carbonates is the main mechanism by which the CO<sub>2</sub> levels of the atmosphere are controlled.
- Point sources of CO<sub>2</sub> 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, e.g. in construction materials, in order to make this process economically more attractive.
- 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.

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(Received 19 February 2004; in revised form 21 February 2005)