Personal code: `328c5SchR.D`

Climatic Change, .(2006), **74**, nrs 1-3, p.349-354.

Enhanced weathering; an effective and cheap tool to sequester CO_2

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Abstract

Weathering and subsequent precipitation of Ca- and Mg-carbonates are the main processes that control the CO_2*-concentration in the atmosphere. It seems logical, therefore, to use enhanced weathering as a tool to reduce rising* CO_2*-levels. This can be applied as a technology, by reacting captured* CO_2 *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_2*-levels of the atmosphere will be adopted more readily if they also serve some broader economic goals. An effective strategy for* CO_2 *control will require many parallel approaches simultaneously.*

Keywords: CO_2 sequestration, olivine, weathering, geochemical engineering

1. Introduction

The fact that Venus has a dense CO_2-atmosphere, whereas CO2 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_2 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_2 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_2 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_2, because chemical weathering can be described by the general equation

$$\text{fresh silicate rock} + H_2O + CO_2 \rightarrow \text{soil} + \text{cations} + HCO_3^- \qquad (1)$$

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_2. 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_2

The recent build-up of the concentration of CO_2 brought about by the rapid combustion of fossil fuels is a cause of concern, and attempts are being made to store CO_2 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_2 in coal beds and enhanced recovery of oil and gas by using CO_2 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_2-levels in the atmosphere down.

This oversight is probably due to the fact that people are unaware of its potential for CO_2-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^{-4} gram of H^+. In 30 years every square meter receives 30 x 7.5 x100

dm^3 x 10^{-4} g H^+/dm^3 = 2.25 g H^+. To neutralize this with olivine, according to reaction (2) 2.25/4 x 140 g olivine is needed, equivalent to 80 g olivine/m^2, 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_2 currently in the atmosphere. Evidently, this reaction would never go to completion, because it would slow down the more the CO_2 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_2. In order to neutralize 5 kg of CO_2 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

$$(Mg,Fe)_2SiO_4 + 4\ CO_2 + 4\ H_2O \rightarrow 2\ (Mg,Fe^{2+}) + 4\ HCO_3^- + H_4SiO_4 \qquad (2)$$

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_2.

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.

3.1 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 Lieftink (1997). In direct analogy to this process it was found that under the right conditions ground olivine reacts with compressed CO_2 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_2. It is stated that " the cost of the process compares favorably with that of competing approaches". In this way large amounts of CO_2 can be fixed. If concentrated sources of CO_2 can be captured at their point of origin (refineries, power stations), then this technology should be capable of preventing the CO_2 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_2, 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_2 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_2-neutral, as can be seen from reaction (3).

$$CaCO_3 + CO_2 + H_2O \xrightarrow[\text{(on land)}]{} Ca^{2+} + 2\ HCO_3^- \xrightarrow[\text{(in the oceans)}]{} CaCO_3 + CO_2 + H_2O \quad (3)$$

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_2 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 meter 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_2, which would make this a rather expensive route for CO_2 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_2 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 ($KMgPO_4.6H_2O$, Schuiling & 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_2 sequestration “anywhere” in the Earth system, it should be made possible to collect a premium for the removal of CO_2 under the provisions of the Kyoto protocol. It will probably be necessary, however, to prove the extent of CO_2 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_2 levels of the atmosphere are controlled.
- Point sources of CO_2 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_2, 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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Utrecht, January 6, 2005

To the Editor of CLIMATIC CHANGE
Dr.Stephen H. Schneider
Professor, Department of Biological Sciences
Stanford University
Stanford, CA 94305-5020

Dear Dr.Schneider,

Thank you for your letter this morning, announcing the acceptance of our paper on Enhanced weathering.
I send you herewith 2 hard copies and an electronic diskette of the final version. I have added a sentence as suggested by you at the end of the abstract.
I have included 4 key words after the abstract.
I also include the signed Consent to Publish form.

With kind regards

Prof.Dr.R.(Olaf) D. Schuiling

Short communication

Coastal spreading of olivine to control atmospheric CO_2 concentrations: A critical analysis of viability. Comment: Nature and laboratory models are different

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article info

Article history:
Received 29 September 2009
Received in revised form 19 April 2010
Accepted 22 April 2010
Available online 24 May 2010

Keywords:
CO_2 sequestration
Olivine
Weathering
Biota

The conclusion of Hangx and Spiers (2009), commenting on Schuiling and Krijgsman (2006), that in the coastal zone up to 2100 years may be needed for 300_olivine sand to be chemically weathered under the uptake of CO_2 grossly understates the uptake rate in natural settings, where flora, fauna and physical processes accelerate the weathering of olivine.

Since some 3 billion years the surface of the Earth has been colonised by biota which stimulate chemical weathering. The sharp decline in atmospheric CO_2 during the Devonian (416–359Ma BP) is ascribed to the colonisation of the continents by deep-rooted trees (Berner, 1992). Mycorrhizal fungi living in symbiosis with plant roots actively extend into the soil and forage for nutrients by altering minerals through acidification and by the release of lowmolecular weight organic chelators (Landeweert et al., 2001; Taylor et al., 2009), to the extent that, e.g. olivine grains (from nearby sources) are not commonly found in soils (Wilson, 2004).

In the coastal zone, grain-to-grain collisions, due to waves and currents, polish reaction-inhibiting Si-rich olivine-surface layers which – under static laboratory conditions – limit the reaction rate. A simple laboratory experiment, in which olivine grains in a closed volume of water are shaken continuously, shows a 4–8% decrease in olivine weight within 1 week, while the pH rises to 9.6 within a few days (authors' unpublished results). Collisions and scraping of the dissolving olivine grains thus enhance the reaction so that it is faster than theoretically predicted on basis of the dissolution kinetics of olivine in (sea)water. This explains why easily weatherable minerals like olivine are commonly absent or underrepresented in the lower reaches of rivers dissecting olivine-bearing source terrains.

In the coastal zone, sediment feeders such as the lugworm (Arenicola marina) are active. They feed on sand grains, up to 2mm in diameter (Cadée, 1976), for bacteria and diatoms. Passage of sand grains through the animal's digestive system may accelerate olivine weathering by 2–3 orders of magnitude (cf. Needham et al., 2006; Worden et al., 2006). Of course lugworms do not rework the complete coastal zone continuously, and this extreme acceleration factor cannot be extrapolated over the full coastal zone. Admixtures of olivine to intertidal areas where lugworms and other sediment feeders are active, may have a positive feedback whereas silica (liberated during olivine weathering) often is a limiting nutrient for the growth of diatoms which in their turn serve as food for sediment feeders.

Chemical weathering of the Deccan Traps shows CO_2 consumption rates of $0.58–2.54\times10^6$ mol/km^2/year (Dessert et al., 2001). Dissolved solid concentration in river waters, induced by basalt weathering on the Island of Réunion indicate CO_2 consumption

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rates of $1.3–3.4\times10^6$ mol/km^2/year (Louvat and Allègre, 1997). Such values are equivalent to the consumption of up to 130 tonCO_2/km^2/year. In mine dumps of crushed ultramafic rocks, consumption of more than 4000 tonCO_2/km^2/year has been measured (Wilson et al., 2009).

In analogy to these natural processes, deep ploughing in humid tropical areas with an ultramafic subsurface and spreading of olivine and other crushed (ultra)mafic rock material over agricultural land will contribute to a reduction of CO_2 levels and, in addition, serve as Mg fertilizer. When used in agriculture in warm humid climates, it can, when carbon credits are applied, support the income of farmers in developing countries. Distribution of olivine and other ultramafic rocks in high-energy coastal systems will counteract atmospheric CO_2 increase and acidification of the marine environment, a serious treath indeed (Orr et al., 2005; Hoegh-Guldberg et al., 2007).

doi:10.1016/j.ijggc.2010.04.012

Certain olivine occurrences indeed contain fibrous serpentine minerals, asbestos (Hangx and Spiers, 2009), and others do not. Olivine is used nowadays, instead of quartz sand, in sand blasting in order to prevent silicosis. This would not be done in case of asbestos admixtures. If needed, technological advances may offer possibilities to neutralize or remove asbestos, e.g. by separation based on specific gravity (asbestos ~1.6 versus olivine ~3) and other treatment.

The energy penalty, i.e., the CO_2 produced by the extra fuel to be burnt for mining, grinding, transport and distribution of olivine is about 4% of the amount of CO_2 captured. Estimates about the energy penalty of CCS (a Faustian Bargain? Spreng et al., 2007) differ, and upstream and downstream consumption, and energy costs of infrastructure are not generally included in such estimates. An additional energy consumption of 25% on a life cycle analysis basis, which might be difficult to achieve (Page et al., 2008; House et al., 2009), requires one additional power plant for every four in use. A significant increase in coal consumption in case of very large-scale CCS deployment will lead to a substantial additional need for coal, and to a lesser extent for natural gas and oil. Even if fuel resources will turn out to be sufficient in the long run, the energy penalty associated with CCS deployment will raise energy prices and price volatilities. This, in turn, may impact adversely the economics and politics of hydrocarbon-rich and hydrocarbon-importing countries (Jansen and Seebregts, 2010; pp 1656–7).

The olivine option, in the coastal zone and on the land, is a cost-effective way to counteract the increase of CO_2 level in the atmosphere, at the same time mitigating ocean acidification. The volume of olivine needed for the neutralisation of human fossil fuel burning is ~7km^3/year, that is about 1m^3/human. This is a large amount indeed, but comparable to the volume of fossil fuels which mankind burns annually, expressed in oil equivalent~10km^3/year, i.e., ~1.4m^3/human. Olivine is produced in open pit mines, while hydrocarbons are often retrieved from kilometres depth in often remote areas.

Olivine weathering is a natural process that takes time, years to decades when applied to suitable environments. Contrary to CCS, the effect is not instantaneous, but in the course of the coming decades in which society will continue to produce CO_2 and to be threatened by continued greenhouse warming, the annual addition of large volumes of olivine to suitable environments will counteract the rise ofCO_2 level of the atmosphere and the acidification of ocean waters.

Acknowledgments

We greatly appreciate the advice of reviewer Klaus S. Lackner and editor Stefan Bachu.

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Chapter 2

MINERAL SEQUESTRATION OF CO_2 AND RECOVERY OF THE HEAT OF REACTION

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Abstract

Apart from saving energy, sequestration of CO_2 is the most direct way of combating the excessive greenhouse effect. Current approaches focus mainly on CO_2 storage in gaseous form in abandoned gas fields or aquifers. Sequestration in mineral form is still in its infancy, because the dry carbonation of common Mg-or Ca-silicates is unsuccessful. It can be deduced from natural examples that wet sequestration, combining hydration and carbonation is likely to be more successful. Several approaches are explored in this paper, either *in situ* in dunite massifs (olivine-rich rocks), or by reacting crushed olivine off-site in contained spaces with the off gases of thermal plants. The reaction produces a large amount of heat, which can be recovered as high enthalpy steam. In order to be effective, however, it should only be applied to large volumes of olivine, in a typical macro-engineering fashion, as the heat losses become unacceptably high in small systems with a high surface to volume ratio. One possibility would be to fill half of abandoned deep opencast mines with ground olivine and cover it by backfill. In the bottom part a mixture of hot CO_2 and steam is injected in order to set up a convective system similar to geothermal systems.

Key words: dunites, mineral carbonation, heat of carbonation and hydration.

Introduction

Olivine-rich rocks known as peridotites or dunites are found in many locations in the world. The major olivine mines are in Norway, but olivine is also produced in Spain, Italy and Turkey. Olivine is a Mg-silicate with the formula Mg_2SiO_4. In natural olivines a small part of the magnesium is always replaced by divalent iron. These rocks originally stem from the mantle of the earth (a 2,900 km thick shell situated between the Earth's crust and the core) that consists mostly of the mineral olivine. In view of the availability of very large masses of olivine-rich rocks, many attempts have been made to sequester CO_2 by reacting it with olivine, but such attempts at dry reaction have failed (Lackner, 2002), or require a pre-treatment at high temperatures to make the MgO available for carbonation in a subsequent step (Kohlmann et al. 2002). A review of technologies for mineral sequestration of CO_2 has recently appeared (IEA Greenhouse Gas, 2005, and references therein). In this report it is confirmed that dry carbonation is not successful, and that so far all technologies for mineral sequestration of CO_2 are uneconomical, but that the direct aqueous carbonation route has the best prospects. Nature also suggests that a two-step reaction might be more favorable. When hot fluids pass through olivine-rich rocks at shallow depth, the rocks are transformed into a mixture of serpentine and magnesite (for the chemical formula of these minerals, see the reaction equation below).

The accompanying photograph (fig.1) of a hand specimen from a dunite at Orhaneli/Turkey demonstrates this phenomenon on a small scale. It shows a lens of chromite ore in a dunitic host rock. The chromite lens shows a number of parallel tension cracks filled with white magnesite. At the places where the cracks pinch out into the dunite rock, the dunite has reacted to form serpentine. Obviously, the fluids that cause these reactions are mainly mixtures of water and CO_2 in varying proportions.

$$\underset{\text{(olivine)}}{2\,Mg_2SiO_4} + CO_2 + 2\,H_2O \rightarrow \underset{\text{(serpentine)}}{Mg_3Si_2O_5(OH)_4} + \underset{\text{(magnesite)}}{MgCO_3} \qquad (1)$$

The reaction has been experimentally verified in an autoclave, where fine-grained olivine was kept in a water-saturated steam mixture at 200°C and a pressure of CO_2 of 36 bar for 24 hours. The X-ray pattern of the products showed clear reflections of serpentine and magnesite, and from the consumption of CO_2 during the experiment it can be judged that the reaction had proceeded approximately 10%.
Because the process offers a possibility to sequester CO_2 in mineral form, and recover the associated heat of reaction, a patent application has been filed at the patent office ("Octrooicentrum") of the Netherlands, entitled "Underground storage of CO_2 with geothermal effect" (Schuiling, 2005).

The reaction releases a large amount of heat

This can be easily understood from the fact that water in the crystalline lattice of serpentine and CO_2 in magnesite are in a well-ordered position, so their thermodynamic properties are similar to those of ice and solid CO_2. It is well known that the melting of ice followed by the evaporation of water, as well as the burning of limestone cost a large amount of energy. If the reaction is going in the opposite direction, forming hydrous silicates and magnesium-carbonate, this same amount of heat is set free. The importance of hydration energy as a possible contribution to heat flow was pointed out in 1964 (Schuiling, 1964 a and 1964 b). The thermodynamic data at 500 and 700 K are as follows (Robie et al., 1978):

	ΔH (kJ/mol)-500K	ΔH (kJ/mol) – 700 K
CO_2	- 393.7	- 394.0
H_2O	- 243.8	- 245.6
Mg_2SiO_4	- 2170.2	-2168.1
$Mg_3Si_2O_5(OH)_4$	- 4360.9	-4352.6
$MgCO_3$	- 1112.0	-1109.2

Table 1: Enthalpies at 500 and 700 K of components participating in the serpentine/magnesite reaction

This means that the reaction as written releases 250.3 kJ per 280 gram of olivine, or 890 Joules per gram at 500 K and a very similar value (240.4 kJ) at 700 K. As the specific heat of ultramafic rocks like dunites is of the order of 1250 $J.kg^{-1}.K^{-1}$ (Landolt-Bornstein, 1985), this means that a pure olivine rock would heat itself by 712°. In real life, however, the temperature will not rise above ~ 500°C, because the equilibrium temperature of the reaction is around 500°C, and part of the heat is required to raise the temperature of the introduced steam and CO_2. If this man-made geothermal energy can be recovered, it qualifies as very green energy, because it is associated with a negative CO_2-emission!

CO_2 sequestration

It can also be seen from the above reaction equation that we can sequester 44 gram of CO_2 with 280 gram of olivine (mol.wt olivine is 140). Even a not exceptionally large dunite massif like Orhaneli, NW Turkey (Orgun et al., 2004) contains already in its top kilometer several tens of billions ton of olivine, by which in the order of several billion ton of CO_2 can be sequestered in mineral form. This CO_2 is permanently fixed, in contrast to sequestration of gaseous CO_2 in aquifers or abandoned gas fields, for which there always remains a chance of escape.

It is interesting to note that one of the largest thermal power plants of Turkey, using lignite, is situated at a short distance from this dunite.

By capturing the off-gases of this plant, that consist mainly of steam and CO_2 (and nitrogen, of course), and injecting them down a borehole into the dunite at a depth of several hundred meters, one can start the reaction described above. While the CO_2 is fixed in mineral form, the temperature of the rock rises, and after some time it should be possible by using heat exchangers to tap this geothermal energy in the form of high enthalpy steam.

Problems

Although this scheme sounds attractive, it encounters a number of problems. The first one concerns the kinetics of the reaction. At ambient conditions, the reaction is essentially a weathering reaction. Olivine weathers relatively fast as compared to other silicates (Schuiling & Krijgsman, 2006), but even so the reaction rates near room temperature are much too slow to be of interest from a technological point of view. Even at 200^0C with fine-grained olivine (120 μ), no more than 10% of the olivine had reacted in 24 hours.

There are two, possibly three ways, however, to increase the rate of reaction. One should, first of all, raise the initial temperature of the system. As a rule of thumb, most reaction rates more or less double for each ten degree temperature rise. This means that a reaction that would take 100 years to complete at ambient temperatures would take only a month at 110^oC. Secondly, the available surface of the reactants should be increased as much as possible, which means that the rock should be crushed and ground as finely as possible, or that the slimes of olivine mining operations should be used. Thirdly, if the gas mixture of steam and CO_2 to be injected contains any sulfuric acid or SO_2, this could be an advantage as well, because olivine dissolves fairly rapidly under acidic conditions (Jonckbloedt, 1997). It has been observed that the dissolution rate of olivine is barely affected by the CO_2 pressure, but the major parameter governing basic silicates dissolution is the pH of soil solutions in contact with minerals (Golubev et al. 2005). A higher initial acidity of the fluid leads to a rise of the Mg^{2+}-concentration in the pore fluid. After this acid is neutralized by further reaction with olivine, the resulting high Mg-concentration in the fluid is expected to enhance magnesite precipitation.

Another type of problems concerns the logistics. It will not often be the case, such as in Orhaneli, that dunite massifs are found in close proximity to large thermal plants. This means that one either has to move the CO_2 to a location with olivine, or the olivine to a location close to a thermal plant. Although one could check the possibility of transporting CO_2 in empty LNG tankers on their return trip, it will usually be necessary to transport the olivine.

In cases where crushed olivine must be transported and used in other locations, this will require a good thermal isolation of the volume of olivine to be reacted. If abandoned deep mines are used, it will also require enough backfill on top of the olivine in order to withstand the pressure of the injected high-pressure steam. The pressure of saturated steam at 250^0C is about 41 bar, so the backfill should have a thickness of about 200 meter (at a specific mass of the rock of 2,000 kg/m^3) to withstand this.

Consequences for implementation

If a thermal plant (or any other point source of CO_2) is close to a dunite massif, the off gases should be transported without cooling through an isolated pipe and injected into the dunite. One can search for tectonically crushed zones in the dunite and inject the gases in such a crushed zone. Unfortunately, nature in most cases will already have preceded us and will have altered these crushed zones and precipitated the same mixtures of serpentine and magnesite. The other possibility is to artificially crack a volume of fresh dunite by hydrofracturing or explosives, or to fill an underground mined-out cavity in the dunite with olivine dust and rubble. The reaction products occupy a larger volume than the original dunite, so some additional cracking of the rock may take place as a consequence of the reaction itself.

If the olivine must be transported close to the site where the CO_2 is produced, the operation of the system becomes complicated. One either needs huge pressurized vessels (industrial autoclaves) or a large underground cavity, where the surrounding rock can act both as a thermal isolator and as a pressure vessel.

Such underground cavities may take many forms. It would be an advantage to have underground cavities that are no longer in use, and even may have a negative value. One can think of cavities produced by solution mining of salt. For safety reasons, to prevent subsidence or even caving in, these must remain filled with saturated brine and indefinitely pressurized. Filling them with fine-grained olivine will push out an equivalent volume of brine, which can be recovered. Hot CO_2 will then be injected into the mixture of olivine grains with interstitial brine. Because the volume of serpentine + magnesite is larger than the volume of the olivine, the pore space between the olivine grains begins to be gradually closed, and the solid reaction product can support the cavity, obviating the need for further pressurizing and monitoring. Once the reaction is underway, the produced heat can be tapped by exchanging it from the solid rock to water circulating in pipes through the system.

Other possibilities involve the use of abandoned deep opencast mines. In most countries regulation requires that these holes in the ground are filled again and the landscape is rehabilitated after the ore deposit is mined out. A deep opencast dunite mine would obviously be the most appropriate choice, but such mines don't exist yet, as far as known. Several examples of deep open cast mines are diamond, copper, molybdenum and lignite mines. In the area between Cologne and Aachen in Germany, for example, several open pit lignite mines reach depths of over 500 meter. After the lignite is mined, these holes have to be filled again. Most of the lignite here is burnt in huge thermal power plants nearby. If one fills the bottom one to two hundred meters of the open-cast pit with ground olivine, lays out a tubing system for heat exchange while dumping the olivine, and then covers the top part of the pit with the original mining waste, the whole system can act as a huge reactor vessel. The backfill, of which the pore spaces are filled for the most part with ground water provides the required containing pressure, and the rock material surrounding the olivine provides an excellent thermal isolation. Part of the cost of filling the lower half of the abandoned pit with olivine can be offset against the costs required to fill the mine anyhow. If an opencast lignite mine with a length of 2 kilometer and a width of 1 kilometer is filled with a layer of 200 meter of olivine, it can sequester approximately 160 million ton of CO_2, and produce in the order of 150 billion kWh (note, however, that this is a non-realistic maximum, as it supposes that the complete heat of reaction can be recovered and converted to electric power).

Using huge abandoned holes as natural reactor "vessels" is a typical macroengineering approach to mineral sequestration of CO_2. A major advantage of using natural cavities instead of huge industrial autoclaves is the fact that reaction kinetics do not play a major role. It is irrelevant whether the reaction proceeds in a few months or a few minutes, whereas reaction times must be as short as possible (preferably an hour or less) if expensive equipment like an industrial autoclave has to be used. This means that reaction times of 1,000 to 10,000 times longer than in an industrial autoclave are still acceptable. If even those reaction times are too short, one can trigger the process by placing a material that reacts faster with CO_2 (like steel slags, slags from the phosphorus industry or incinerator ashes) and also produces heat at the center of the olivine. This will locally increase the temperature, which in turn will speed up the olivine reaction.

A major disadvantage of the proposed sequestration technology is the fact that only one out of four Mg-ions that are made available as olivine is used for CO_2 sequestration, whereas the other three are used to make serpentine. This places a heavy burden on the transport costs of olivine, when it has to be transported off-site to a thermal power plant. A second disadvantage is that the reaction products are mixed together, which makes it virtually impossible to use the products.

Evidently, a reaction like

$$Mg_2SiO_4 + 2\ CO_2 + 2\ H_2O \dashrightarrow 2\ MgCO_3 + Si(OH)_4 \quad (2)$$

would considerably improve the economy of mineral sequestration, as all Mg-atoms are converted into magnesite. One could think of the following process. A long pressure vessel is heated at one end, whereas the other end is kept at a lower temperature. The olivine is loaded at the hot end, and a mixture of CO_2 and steam in a 1:1 molar ratio is added to the charge. The solubility of SiO_2 in water of 300^oC is in the order of 1 wt% (10,000 ppm, Fyfe et al., 1978), whereas amorphous silica has a solubility of about 100 ppm at room temperature. Although no data on the variation of the solubility of magnesite with temperature are available, by analogy with Ca-carbonate (Fyfe, 1978) it can be expected that magnesite also becomes less soluble at high temperatures. This would mean that SiO_2 and $MgCO_3$ might precipitate at different places in a pressurized system with an imposed thermal gradient. Due to this gradient, there will be convection in the fluid. At the cold end of the vessel the SiO_2 will precipitate when the fluid cools, so the return water is strongly undersaturated when it comes again into contact with olivine at the hot end. More olivine will dissolve, and the Mg-concentration of the fluid will increase up to the point where magnesite starts to form. It is expected that the precipitation of magnesite will proceed more easily when carbonate and magnesium ions are both present in solution than in the case where a magnesium oxide or hydroxide must be carbonated. This is the case for many of the proposed mineral sequestration schemes that also use olivine rich rocks, but where Mg-oxide or hydroxide is first extracted from the rock (e.g. Lackner et al., 1997). If one can make the magnesite to precipitate in a different part of the pressure vessel than the silica, which is likely if their behavior is as predicted, it is possible at the end of the run to recover magnesite and precipitated silica separately, and use them as valuable products. Even if this turns out to be impossible, the proposed method has the advantage that all the magnesium of the olivine is converted to magnesite, by which the economy of the sequestration is improved fourfold.

This process also has its counterpart in nature. In many magnesite deposits like the magnesite deposits in the ultramafic rocks on the Kassandra Peninsula, the westernmost peninsula of Chalkidiki, Greece, it can be seen that the magnesite veins have formed in fissures of the host dunite, while at the same time extensive silicification has taken place, with precipitation of opal-like phases. The difference between the two processes in nature is probably that the reaction leading to the association of serpentine + magnesite takes place in a more or less closed system, whereas the combination magnesite + opal forms in open systems close to the earth's surface, which is also suggested by the observation that the magnesite veins become rarer and thinner towards depth. It would be worthwhile to see if we can create similar process conditions as in these magnesite deposits.

It is conceivable that a half open system as described for the abandoned lignite mines, in which the fluid is permitted to convect through the olivine grains between the hot bottom part and the cold top part could produce a similar result, and will possibly result in a silicified caprock. This in turn makes it possible to recover the heat of carbonation more completely. In fact, the reaction in which only magnesite and precipitated silica are formed seems to produce even more heat than the combined serpentine + magnesite reaction, as can be seen from the accompanying table.

Compound	ΔH (298), kJ/mol
CO_2	- 303.5
H_2O (ideal gas)	- 241.8
Mg_2SiO_4	- 2170.4
$Mg_3Si_2O_5(OH)_4$	- 4361.7
$MgCO_3$	- 1113.3
$Si(OH)_4$	- 1460.0

Table 2: Enthalpies at 298 K of components participating in reactions (1) and (2)

For reaction (1) the enthalpy of reaction is calculated as –257.1 kJ (compare to –250.3 at 500 K and – 240.4 at 700 K), whereas the enthalpy of reaction (2) after it is normalized to two olivine in order to make it comparable, comes out as -490.2 kJ, almost double the heat of reaction of the reaction leading to magnesite + serpentine.

Many of the parameters to operate such a system (rates of reaction, olivine grain size, optimum temperature and optimal temperature gradient) are not, or only poorly known, and will require extensive experimental study.

The energy production, and the CO_2 emitted or immitted per ton of raw material are summarized in table 1. Although the energy produced by the mineral sequestration of CO_2 per ton of olivine is modest, although not insignificant compared to coal, it becomes quite important if the comparison is based on balancing the CO_2 emitted by coal combustion with an equal amount of CO_2 sequestered by olivine.

	energy produced	CO_2 emission/immission
1 ton of coal	~ 29,300 MJ	~ + 2,830 kg
1 ton of lignite	~ 17,000 MJ	~ + 1,200 kg
1 ton of olivine (reaction (1)	917 MJ	- 157 kg

1 ton of olivine (reaction (2)	1,750 MJ	- 628 kg

Table 3. Energy production and CO_2 impact of raw materials discussed in this paper.

If all the CO_2 produced by the combustion of olivine is sequestered by reaction (1), it would require 18 tons of olivine, and produce 17,500 MJ. If the sequestration is done by reaction (2), it would require only 4.5 tons of olivine, but produce less energy, namely 7,900 MJ. This means that at locations where olivine resources are nearby and abundant, reaction (1) is to be preferred, whereas in situations where the transport costs of olivine dominate, reaction (2) would be more economical.

Conclusions

Dunitic rocks, or the olivine contained in them offer the possibility to sequester large volumes of CO_2 by applying a combined hydration/carbonation approach.

The heat of reaction from the reaction by which olivine is converted to serpentine + magnesite is substantial and can be recovered.

It is worthwhile to study a non-equilibrium process, where olivine is subjected to a thermal gradient in a convecting mixture of steam and carbon dioxide. This permits a more efficient use of the olivine for the mineral sequestration.of CO_2, because all the magnesium is converted to $MgCO_3$.

Many of the parameters governing the reactions as described are not, or poorly known and will require extensive experimental studies.

The macroengineering approach outlined in this paper makes use of large man-made holes as pressure vessels for mineral sequestration and bypasses the problem of poor kinetics that must be faced when huge and expensive industrial autoclaves are used.

If the reaction leading to magnesite + amorphous silica can be successfully applied in deep opencast mines, it may represent a breakthrough to the solution of the greenhouse problem, as the recovered heat of reaction is substantial, compared to the power produced by the combustion of fossil fuels.

Acknowledgments

I wish to thank Mr.Koral Korkut of SETAT Mining company for his kind hospitality at the olivine mine near Orhaneli. I also thank Prof.P.Krijgsman for carrying out the experiment leading to the partial conversion of ground olivine to a mixture of serpentine and magnesite. Thanks also to Wouter .Huijgen and Prof Rob Comans of the Energy Research Center of the Netherlands (ECN) for their review.

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