Weathering Approaches (Enhanced) for Carbon Dioxide Sequestration for mitigation of climate change and ocean acidification.

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1. Definition of the subject

The aim of enhanced weathering is to capture CO2 by the carbonation of silicates, or by dissolution of these silicates during which the greenhouse gas CO2 is converted to bicarbonate in solution. Research in this field is still focused on increasing the rate of reaction, but the required additional technologies add considerably to the cost of the process. In this chapter the focus is on the optimization of the weathering conditions, by selecting the most reactive abundantly available minerals, grinding them and spread the grains over land. Thereafter nature takes its course.

Since its formulation in the late nineties, more and more people realize that this simple and natural approach may well turn out to be one of the most promising and environmentally friendliest ways to counteract climate change and ocean acidification.

2. Introduction

CO2 is a greenhouse gas. The rising concentration of CO2 in the atmosphere by the burning of fossil fuels is considered by many to be the main cause of climate change. Most efforts on carbon sequestration so far have focused on the physical removal of CO2, by locking it up as a supercritical fluid in available spaces in the subsoil, like abandoned oil and gas fields or aquifers. Sequestration by mineral carbonation* has long been neglected, as it was deemed to be too slow or too costly. The main arguments for a slow rate of reaction stem from an extrapolation of abiotic experiments in the laboratory. Observations from the "real world" only now begin to show that weathering rates are often 1 to 2 orders of magnitude faster than rates determined in the laboratory. Arguments based on the apparent high cost aspect are due to the fact that almost all researchers assume that mineral carbonation must be coupled to a technology to speed up the reaction. This may involve thermal treatment of the mineral, a chemical or mechanical pretreatment or a technology based on subjecting the mineral to high pressures and temperatures in

autoclaves. Most of these approaches are successful to some extent, but their high cost makes such mineral carbonation technologies unattractive (1), and some produce large amounts of CO2. If there is no objection to the reaction taking a few months or a few years to run to completion, then there is no need for the use of expensive equipment, which must meet minimum throughput rates for financial reasons. Given these conditions, chemical weathering in favorable environments becomes an attractive proposition. It can be applied on a world scale, it is a low-cost operation per ton of CO2 captured, it is sustainable, it provides employment opportunities in developing countries, and unpleasant environmental surprises are unlikely, as the same process has already operated over the entire geological history.

This chapter, therefore, will focus on the enhancement of the process of chemical weathering, by which a mineral is converted to a bicarbonate solution. These bicarbonate solutions are transported by rivers to the oceans, where they will be captured as carbonate rocks, which are the ultimate sink for CO2. During the precipitation of solid carbonates, half of the CO2 is released again, but this process takes on average several hundreds to thousands of years, so the bicarbonate step is the relevant step for climate change mitigation.

Keywords

Enhanced weathering; CO2 capture; dunite mining; olivine spreading; weathering rates; nickel laterites; employment in developing countries; geopolitical implications

Glossary of some terms

Mineral carbonation: the reaction of CO2 with minerals (particularly Mg- or Ca-silicates), leading to the formation of solid and stable carbonates. This carbonation is preceded by the transformation of CO2 gas to bicarbonate solutions.

Weathering: the process whereby rocks are decomposed by reaction with water and acid (usually carbonic acid)

Enhanced weathering: Any process whereby weathering reactions are speeded up, like crushing the rock into fine particles and spreading these in suitable climates.

Laterite: iron-rich tropical soil, which is the insoluble residue left after the weathering of

Dunite: common rock type consisting for more than 90% of the mineral olivine. Olivine: a silicate which is a mixed crystal of Mg2SiO4 and Fe2SiO4. It is the fastest weathering common silicate.

CO2 capture: any process whereby CO2 is sustainably removed from the atmosphere for a long period. It is doubtful whether the planting of trees conforms to this definition.

3. Capturing CO2 from industrial point sources or from the atmosphere?

The focus so far was to capture the CO2 from point sources (flue gases from coal-fired power plants, cement factories, refineries, steelworks, fertilizer plants). An additional argument was that nations wanted to capture their "own" CO2. The atmosphere, however, is a well-mixed reservoir on a time-scale of a few months, and all molecules of CO2 are equal, so it makes no difference where the CO2 is captured, nor what its origin is as far as its effect on climate change is concerned. The goal of mankind in its attempt to combat climate change must, therefore, be defined as follows:

Mankind should aim to capture as much CO2 as possible in a safe and sustainable way, for the lowest cost, anywhere in the world and independent of origin

This chapter will focus on the application of enhanced weathering of silicates It is a natural and sustainable mechanism, as weathering has throughout geological history been the main controlling mechanism for the level of atmospheric CO2. It is considerably cheaper than all technologies proposed so far, like the capture of CO2 from flue gases, purifying it, compressing it and injecting it in abandoned gas fields or aquifers, or similar expensive technologies.

It is difficult to grasp the scale of the problem. Present annual anthropogenic emission of CO2 is more than 25 billion tons (2). By whatever means this CO2 is captured, it will require equivalent volumes of reactants. This requirement means in practical terms that the materials to be used for CO2 capture must be cheap and widely available.

4. Materials

Most materials to be used for carbonation are naturally occurring rocks or minerals, although residues from industrial processes are also considered. Industrial residues have the advantage of being readily available and sometimes need to be removed or treated anyhow, but their total volume is too small to make more than a small dent in the CO2 problem. Even though industrial wastes cannot solve the problem of sufficient CO2 removal on their own, they still constitute an easily accessible and cost-effective part of the solution. Some of the materials in this category are (coal) fuel ashes, oil shale ashes, metallurgical slags, including slags from the production of elementary phosphorus, red mud from the alumina industry and wastes from the demolition of concrete buildings (3,4). It was shown that wastes from the demolition of concrete are rapidly carbonated in soils, and their carbonation compensates for decarbonation during manufacture. If some of the other mentioned materials do not undergo carbonation fast enough by themselves, it may be sensible to help the process along.

In Hungary a dam that contained the red mud sludge of an alumina plant collapsed in 2010. This event was widely discussed in the media; nine people were killed, a huge area in the country was polluted and all fish in the river was killed. It may be wise, as a precautionary measure, to neutralize all storage basins of caustic red mud, which has a pH close to 13, by mixing it with CO2. It can be done by bubbling CO2-rich flue gases through the red mud. Future discharges of red mud could possibly be treated, online, by using pressurized CO2-rich flue gases as a propellant when the red mud is pumped to the basins. This has probably the additional advantage to make desulfuration installations for the flue gases superfluous, as SO2 reacts very fast with the red mud. A likely scenario is that the free NaOH in the red mud will be converted to soda or sodium sulfate, and the pH will be lowered to safe levels. Any remaining alumina in the red mud is expected to precipitate as the mineral dawsonite, a sodium-aluminium carbonate hydroxide The reactions involved are

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(1) 2 NaOH + CO2 \rightarrow Na2CO3 + H2O
(2) 2 NaOH + SO2 + 0.5 O2 \rightarrow Na2SO4 + H2O
(3) NaOH + CO2 + AI(OH)3 \rightarrow NaAICO3(OH)2 + H2O
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Among the naturally occurring materials for carbonation, olivine and olivine rocks, called dunites, take a prominent place, because olivine weathers fast and is abundantly available (see fig.1).

Other candidate materials include basalts and basaltic tuffs, and possibly anorthosites. A mineral that is also frequently mentioned is wollastonite (CaSiO3). Wollastonite does react fast with CO2 and water, but wollastonite deposits are rare and small, so the mineral does not offer a solution for massive removal of CO2 from the atmosphere. It is evident that priority will be given to material that is already crushed or milled, as this saves mining and milling costs. Many ore deposits of chromite, nickel, magnesite, peridot (a semi-precious variety of olivine), or even diamond have olivine-rich host rocks. Billions of tons of such rocks can be found in crushed form as mine tailings, and using these saves the cost of mining and milling the material, and clears the sites where these mine tailings were stored for other purposes. Later on, in the section on rate of weathering, some spectacular evidence on the rate of weathering of powdered olivine or serpentine (the hydration product of olivine) on mine dumps will be presented.

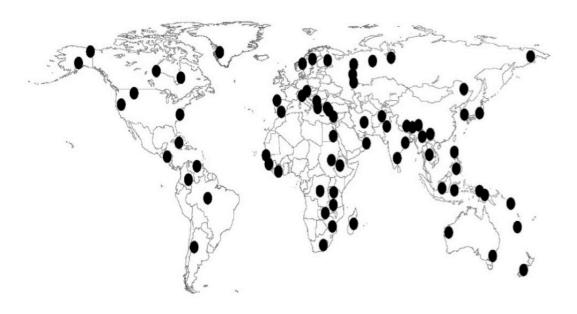


Figure 1: Distribution of dunites in the world. One dot in a country may represent several dunites

5. Modes of application

- 1. In dedicated industrial installations
- 2. In situ injection in suitable rock types
- 3. Ex situ after crushing and spreading suitable rock-types.
- 1. Industrial installations require an input of fairly pure CO2 to reach a maximum result for these installations, because otherwise they would process large volumes of gas which are released again at the end. This means that they are basically dependent on point sources of pure CO2, or on more dilute sources of CO2 from which the CO2 must first be captured and purified. Industrial treatments, involving thermal or chemical activations, or huge autoclaves through which the mineral powders must pass as fast as possible probably have no future to counteract climate change, as they cannot compete with the simpler and much cheaper alternatives under 2 and 3. One evident cost and efficiency aspect is the fact that the processes involved in such industrial installations are counterproductive because they use up a considerable amount of energy themselves. It is doubtful that large-scale application of thermal or chemical treatment of olivine, for instance, can ever be carried out on the required scale of 25 billion tons of olivine annually, let alone in a cost-effective way. The same holds for proposals to inject purified CO2 streams in underground reservoirs.
- 2. In situ injection in suitable rock types. The major distinction between this type of injection and the more commonly proposed CCS (Carbon Capture and Storage) is that injection in flood basalts or olivine rocks aims at converting the injected CO2 gas into carbonate rock by reaction with the host rock. This reaction produces some heat, which may further speed up the reaction. In oil and gas fields, or in saline aquifers the CO2 remains in the reservoir as a gas (or more correctly as a supercritical fluid), with the inherent risk of leakage, or even explosive escape. The sedimentary rock units in which oil and gas accumulations are found are almost exclusively unreactive, mature sediments, from which the reactive minerals have long since disappeared during earlier cycles of weathering and erosion. CO2 stored in such reservoirs with unreactive rocks will remain a gas almost indefinitely, or it will dissolve under high CO2 pressure in the pore fluids, from which it will exsolve like bubbles in a bottle of beer the moment that the pressure drops as a consequence of the opening of a fault or a failure of the installations. This is what recently happened with the CO2 that was injected in the Weyburn field in Canada. It has started to leak, leading to the death by asphyxiation of several animals (as reported in the Dutch newspaper NRC on January 13, 2011).

The main conditions for a reservoir rock in which the CO2 will be injected and converted to solid carbonates are reactivity and, what can be called, "selective" permeability. A combination of these two could theoretically be found in fracture zones in appropriate rock types, but here, unfortunately, in many cases nature has preceded any potential use by mankind. These crushed zones have already often acted as preferential channels for fluid transport. As natural fluids consist predominantly of water + CO2, most of the fragmented rocks have already been carbonated, or carbonates have precipitated in the voids between the rock fragments (see fig.2), reducing permeability and making the rock unfit for CO2 injection. This means that in most cases, once a site has been selected, the permeability of the rock must be artificially increased by hydrofracturing ('fraccing"). Although this is an established technology, it adds considerably to the cost of the operation.

Thick sections composed of many superimposed volcanic flows with a horizontal extension of sometimes more than 1 million km², so-called flood basalts, may be an exception. By the very nature of a lava flow, such flows are often separated from the overlying flow by a rubble zone, which can have high permeability. During the eruption, the top of a lava flow cools fastest and becomes a solid crust. As the lava flow moves on underneath this solid crust, this crust is broken up and forms a permeable layer of broken pieces carried along on top of the lava flow. A second positive factor may be that one often finds a high concentration of bubbles near the top of the flow, representing gas bubbles that were trapped in the lava flow after they exsolved from the lava and moved upward. These bubbles contribute to the accessibility of the rock for rock/fluid interaction. Once the fluids have reached the bubble zone, a large area for reaction becomes available.

A third, and often important property of some lava flows is their vertical, more or less hexagonal columnar jointing that originates from shrinkage during cooling. This permits easy access for fluids throughout the basalt flow. The combination of these properties makes piles of basalt flows almost ideal targets for injection, although their reactivity is considerably lower than that of olivine-rich rock types.

Flood basalts can occupy enormous volumes, in several cases in excess of 1 million km 3 . Well known examples are the Deccan traps in India, the Siberian traps, the Karroo basalts and the flood basalts of the Parana basin, each covering more than 1 million km 2 . Even the more modest Columbia river flood basalts with a volume of "only" 250000 km 3 would be more than enough to capture all the $\rm CO_2$ that is already emitted by mankind, and will be emitted in the near future. The Columbia river flood basalts and the Deccan traps are presently under investigation how they can be used for carbon capture (5). Logistics of CO2 transport and its associated cost, as well as the rate at which it can be injected and the reactivity of the rock will probably limit their use as a CO2 trap to locations close to voluminous point sources of CO2. They clearly constitute a safer storage than aquifers or abandoned oil and gas fields, because after reaction with the rock the CO2 is no longer stored as a gas but as a solid carbonate.

The situation with direct injection into olivine-rich rocks is more or less the reverse of injection into basalt piles. Permeability is often much smaller, as most dunites (dunite is the rock-type that consists for more than 90% of olivine) are massive rocks. They may contain joints, but these are often sealed with a thin veneer of serpentine or magnesite (MgCO3). On the other hand, their reactivity is considerably better.

Spectacular examples (fig.2) of carbonation of olivine-rich rocks in Oman were presented by (6). These authors propose that annually up to 1 billion tons of CO2 can be injected into these rocks in Oman. Transport of such volumes of CO2 from industries and coal-fired power plants in the industrialized world, purifying it and bring it to a remote site poses, however, a huge logistical problem. The required handling and transport certainly does not make this a cheap solution. It has been suggested (Schuiling, pers. comm.) that a part of the logistical problem could be solved by loading CO2 in the same ships that transport LNG (liquefied natural gas) from the Middle East on their return trip, provided the corrosivity of CO2 presents no problem. The ships are already equipped with all the cooling requirements. Even if the logistical problems are not insurmountable in terms of cost, there remains the problem that the rocks must be intensely fracced for injection. Kelemen and Matter suggest that the considerable heat of reaction from the hydration and carbonation (7,8) may help to crack the rocks further.

Although from the reactivity point of view direct injection of CO2 + water into dunites is an attractive proposition, the likely high costs may limit its use to locations where a coal-fired power plant is situated at short distance from a dunite massif like near Orhaneli/Turkey (9), or where, like in Oman, the CO2 produced by the installations on oil and gas fields can be injected directly into the dunites nearby. It may be mentioned in passing, that the slopes of the ophiolite mountains in the desert climate of Oman are covered by a talus of

olivine-rich rock pieces, so it is probably much cheaper to inject the CO2, dissolved under pressure in water into these scree deposits rather than into the solid rock (Schuiling, pers.comm).



Fig.2 Multiple generations of carbonate cement around dunite pieces in alluvial terraces in Oman (6)

3. Ex situ after crushing and spreading suitable rock-types. This option is better known as enhanced weathering (9). This is probably the most promising solution for the sustainable capture of CO2 on the scale of billions of tons of CO2 annually. It is only for this option that a more complete description of the proposed process will be given, as well as some quantitative estimates of its costs and energy requirements. Furthermore the possible collateral benefits of the method will be considered.

6. Geochemical justification for enhanced weathering

The Earth is subject to continual degassing of CO2 (Figure 3). Near the island of Milos, each year 2.2 million tons of CO2 bubble out of the shallow seafloor (10). If this has gone on for the duration of the volcanism in that area so far, which is 3.5 million years, the integrated CO2 emission near Milos from an area of only $35~\rm km^2$ has reached a staggering 7000 billion tons. Many similar areas of diffuse emission of large volumes of CO2 are found in the Mediterranean area, e.g. near Ischia (Italy) and Nysiros (Greece).

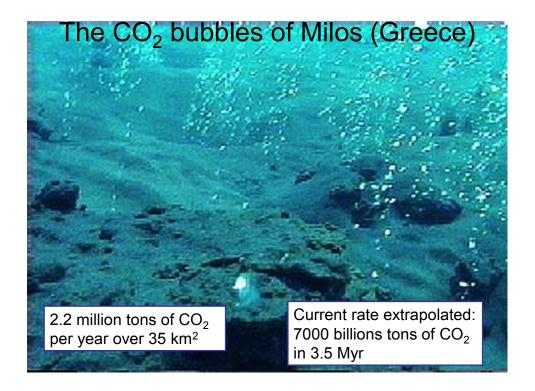


Fig.3: Near the island of Milos each year 2.2 million tons of CO2 are bubbling out of the seafloor.

7. Weathering

It is estimated that the Earth produces around 0.5 billion tons of CO2 each year, mainly from volcanic sources (11). Other important sources of CO2 are carbonate rocks that decompose after having been transported to great depth and subjected to high temperatures in subduction zones (12), or limestones and dolomites in the contact aureole of intrusive rocks, or marbles or siliceous dolomites undergoing high-grade regional metamorphism. If there were no feedback mechanism or mechanisms by which this CO2 is constantly removed from the atmosphere and sustainably stored in rocks, the Earth would now have an atmosphere similar to Venus, where the CO2-pressure of the atmosphere is 80 bars, and the surface temperature of the planet is 460°C, due to the excessive greenhouse effect.

The major feedback mechanism is the weathering of silicate minerals, in particular Ca- and Mg- silicates, which is only possible thanks to the presence of liquid water on Earth, whereas it is absent on Venus. A smaller feedback mechanism is the storage of CO2 as organic carbon (oil and natural gas, coal, and organic carbon dispersed in sediments). Chemical weathering can be described as the neutralization of an acid by rocks. H2CO3 is the dominant acid during weathering. It is converted to bicarbonate in solution. The rock is partly dissolved. A residue of clay minerals can form as the solid end-product. Weathering has been a life saving process for our planet. Not only has the interaction of CO2 and water with rocks saved us from a greenhouse problem as found on Venus, but it has provided us also with fertile soils, without which it would have been impossible for any evolved life forms to develop, and it has released the mineral nutrients from the rocks which are a basic requirement for plant life.

Some typical weathering reactions are as follows

(4) $Mg_2SiO_4 + 4 CO_2 + 4 H_2O \rightarrow 2 Mg^{2+} + 4 HCO_3^- + H_4SiO_4$ (weathering of olivine)

(5) $CaSi_2Al_2O_8 + CO_2 + 2 H_2O \rightarrow CaCO_3 + Al_2Si_2O_5(OH)_4$ (weathering of anorthite)

The first reaction, the weathering of olivine, describes an intermediate step in the weathering process. After this dissolution step the Mg-bicarbonate solution is transported to the sea, where ultimately it will precipitate in the form of carbonate sediments

(limestones and dolomites). That process, however, takes on average hundreds, if not thousands of years, so the first step, the formation of Mg- or Ca-bicarbonate waters is the relevant step for CO2 capture on a time scale of a few tens of years. The second reaction demonstrates the formation of a carbonate and a clay mineral by the weathering of anhydrous silicates.

Many non-geologists think that the CO2 that is dissolved in the oceans, present as CO2 in the air, or contained in biomass plays the major role in the CO2 balance of the Earth. In fact, these reservoirs are only short-lived and minor transitory storage rooms. The major part of the geochemical CO2 cycle is represented by emission of CO2 from the Earth, its transformation by weathering into a bicarbonate solution, followed by its transport to the oceans and deposition as carbonate rocks. These carbonate sediments form the ultimate sink on a human time-scale. Geologically speaking, even these solid carbonate sinks are not eternal, but are recycled as well, albeit with time-scales of hundreds of millions of years. The relations can be demonstrated with the following table (Table 1)

	Amount of carbon (x 10 ¹⁵ kg)	Relative amount (%)
Limestone (CaCO ₃)	35.000	46.6 %
Dolomite	25.000	33.3 %
Sedimentary carbon	15.000	20 %
Recoverable fossil fuels	4	0.005
Oceanic CO ₂	42	0.056
Atmospheric CO ₂	3	0.004
Biomass	0.056	0.0007
Anthropogenic emission	0.03 /year	
Input from Earth's interior	0.002/year	

Table 1: Distribution of carbon on Earth. Modified after (13)

The process of chemical weathering has always provided the main mechanism to keep the CO2 levels of the atmosphere within reasonable bounds. Of course there have been fluctuations in the course of geological history, because the available surface area where reactive rocks were exposed to the atmosphere varied; during or shortly after major orogenic periods, or after large-scale volcanic activity the area of fresh rocks available to weathering was larger than in periods where the landscape was more mature, and where many easily weatherable rocks were covered by a thick weathering crust, which virtually stopped their interaction with CO2 and water. At the same time it is likely that the annual emissions of CO2 from the Earth were also subject to large variations caused by the intensity of volcanism, related to the rate of plate spreading.

To a certain extent such variations are counteracted by the CO2 concentration of the atmosphere itself, which acts as its own negative feedback. The higher the CO2-pressure, the more acid the water, and the faster the weathering which removes that same CO2 from the atmosphere.

There is geological evidence that factors like mountain building or massive volcanism, through their effects on rates of weathering and emission of CO2 have influenced the CO2 pressures of the atmosphere in the past, and may have led to periods of glaciation (14, 15, 16).

Since the industrial revolution atmospheric CO2 levels have risen rapidly (from 260 to 392 ppm), largely due to mankind burning in a few hundred years the fossil fuels that took hundreds of millions of years to form. If weathering is going to be used as a tool to counteract this rise in CO2, caused by mankind annually emitting more than ten times as much CO2 than the Earth normally emits, then the weathering process must also be made more than ten times more effective than normal to reach a new balance. The process as discussed here is to select widely available rock-types that weather easily, mine them and increase their reactive surface area by crushing them, and spreading the crushed rocks over land or along beaches in areas with the most suitable climate for weathering.

In subsequent sections only olivine and olivine rocks will be discussed. Other rock types can also be used, but they are less effective or less available, although locally there may be good reasons to use other rocktypes such as basalts, anorthosites or nepheline syenites. In the following weathering reactions the formula of olivine will be simplified to Mg2SiO4, although olivine normally is a mixed crystal of Mg2SiO4 and Fe2SiO4, with the Mg-endmember usually dominant. One finds a number of ways in which the weathering reaction of olivine is described. As this affects the amount of CO2 that can be captured for a given amount of olivine, these different weathering reactions will be briefly discussed, and the major reaction that takes place in nature will be identified. A common way is the reaction in which during weathering two new solid minerals are formed, namely magnesite (MgCO3) and serpentine (Mg3Si2O5(OH)4)

8 . Weathering reactions of olivine

In this reaction, 2 olivine moles capture 1 CO2.

A second reaction is

(7) Mg2SiO4 + 2 CO2 + x H2O
$$\rightarrow$$
 2 MgCO3 + SiO2.xH2O

In this reaction, 1 olivine mole captures 2 CO2

The reaction that occurs normally in places with sufficient rainfall

In seawater it is convenient to split the reaction into

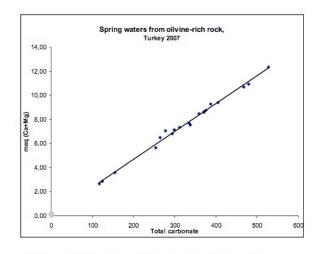
(9a) Mg2SiO4 + 4 H2O
$$\rightarrow$$
 2 Mg2+ + 4 OH- + H4SiO4

followed by

In reactions (8) and (9a and 9b) each olivine mole captures 4 moles of CO2. Evidence will be presented that reaction (8) is the common weathering reaction. It has been mentioned already before that the resulting Mg-bicarbonate waters will ultimately form carbonate rocks in the oceans. During the precipitation of those carbonates, half of the captured CO2 returns to the atmosphere, but as this process may take thousands of years, we will neglect it as far as it affects climate change in the short run.

In order to find out what is the normal reaction mechanism for olivine weathering, a suite of spring waters issuing from olivine rocks in Turkey were collected (17). One can distinguish the following steps during the formation of such spring waters:

- 1. Rainwater falls on the ground
- 2. It infiltrates the soil. The CO2 concentration in soil atmospheres is usually around hundred times larger than in the open air, because litter in the soil decays, and soil fauna respires, both contributing to a high concentration of CO2 in the soil (19,20).
- 3. After equilibration with this CO2-rich soil atmosphere, the water infiltrates the underlying rock, and reacts with it (the weathering step).
- 4. Finally the water emerges again as a spring at some lower point. Olivine-rich rocks contain generally, next to the dominant mineral olivine, some other silicates, including calcium-silicates. From Figure 4 it is evident that there is a close relation between the (Mg + Ca)-content of the water, expressed in milli-equivalents and the amount of CO2 that has been converted to bicarbonate. This close relation has been confirmed in a number of cases all over the world, and it can be concluded that the reaction leading to bicarbonate in solution is the major pathway in which CO2 is removed from the air, taken up as bicarbonate in the water and transported to the oceans.



Concentration in meq [Ca₂⁺ + Mg₂⁺] in spring waters in dunite massifs versus total carbon as mg CO₂

Figure 4: Relation between calcium + magnesium extracted from the rock, and amount of CO2 captured as bicarbonate in spring waters issuing from olivine rocks in Turkey

Even when the problem is considered on the scale of the whole Earth the picture remains essentially the same. All rivers together transport annually 3.6×10^{16} kg of water to the oceans. The weighted average of their concentration of Ca is 11 ppm, of Mg 2.6 ppm and of HCO3 42.4. Expressed again in milli-equivalents this means that Ca+Mg make up 0.77 meq and bicarbonate 0.7, so, despite all complications, there is still a satisfactory agreement. If we calculate from these figures the amount of CO2 that is annually brought to the sea by rivers, this comes out as 1.1 billion tons of CO2, the same order of magnitude as the annual emission of CO2 by the Earth, which is obviously larger, as emissions of CO2 from the seafloor are only partly taken into account. Some of this CO2 returns to land, takes part in weathering reactions, and returns as bicarbonate to the oceans.

9. Enhanced weathering: what does it involve?

Having established that the principal weathering reaction is reaction (8), the formation of magnesium bicarbonate solutions, it can now be calculated from the stoichiometry of this reaction how much olivine is required to sequester each year all the emitted CO2 by enhanced weathering, under the assumption that energy savings, switching to green energy and change of lifestyle will not lead fast enough to a lowering of the world's CO2 emissions, and other technologies for CO2 capture will remain negligible. In this scenario the required volume turns out to be approximately 7 km³ of olivine rock. This is, of course, large, because it must match the carbon contained in all the oil, gas and coal that is burnt. It is, however, within the range of modern large scale mining. This volume of olivine is equivalent to 10 km³ of oil. It is worthwhile to come to grips with the scale of this mitigation effort (fig 5). The largest mine in the world, the copper mine at Bingham, Utah, USA has an excavated volume of 25 km³. Olivine mining at this scale, however, means that olivine moves up from a modest commodity to third place in the mining industry, after construction materials and coal.

One should, obviously, not open only one single, huge olivine mine, but spread the mining operations over 30 to 50 open pit olivine mines. In order to profit from the most suitable climatic conditions for weathering, these mines should be strategically spread along the tropical zone. A larger number of olivine mines will be able to service wider areas without requiring large transport Each of the selected sites for olivine mining must produce in the order of 500 million tons of olivine each year to reach the required 7 km³ per year. It may well turn out that it is more favorable both economically and environmentally to

increase the number of olivine mines, and decrease their size. At the same time this will spread the economical benefits of olivine mining over a larger number of countries, and further limit the required transport distances. This volume of olivine rock must be crushed and milled to grains of around 100 micron diameter. If 7 km 3 is spread over an area of 10 million km 2 , it will occupy a layer of 0.7 mm thickness. In the section on rate of weathering, it will be shown that grains of olivine of 100 micron will weather in approximately 5 years in tropical soils. It will, therefore, be cheaper to spread a layer of 3.5 mm thickness each year over an area of 2 million km 2 , shift to the next area in the following year, and come back to the first after 5 years

In a few instances outside the tropical zone conditions may be so favorable that large olivine exploitations can be located there. For example, a possible site for an olivine mine outside the tropical zone might be Oman, which has the largest ophiolite zone in the world and a long coastline along the Indian Ocean. Deeply weathered sections of dunite, dating from earlier more humid periods can be found, but in its present desert climate, the olivine doesn't weather, but forms huge talus deposits on the slopes of the mountains, at a short distance from the Indian Ocean. These scree deposits have no overburden which must first be removed, like in most tropical dunite deposits. In Oman, the loose pieces, after some additional crushing, can be loaded into ships that have direct access to the Indian Ocean. This would fit in with the aim of Oman to broaden its industrial base when revenues from the oil and gas sector will diminish. An olivine mine in Oman could serve, for example, to supply olivine sand to reinforce the beaches of the Maldives, threatened by sea level rise as a consequence of climate change.

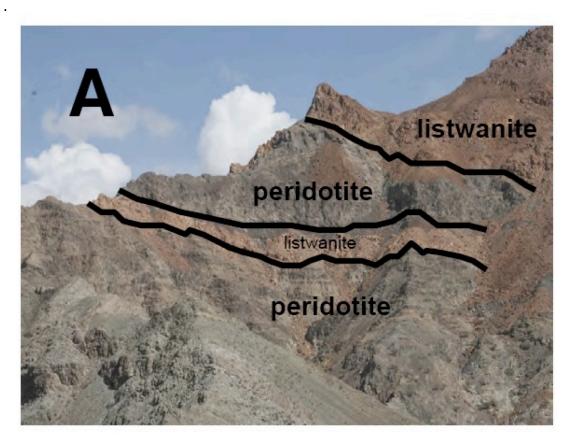


Fig. 5: It is a sobering thought that these huge bands of listwanite (completely carbonated dunites consisting of magnesite +quartz) in Oman, containing 500 million tons of CO2 are equivalent to only one week of the world's anthropogenic CO2 emissions (5)

10. Sequestration of CO2 from natural CO2 emissions

Although natural emissions constitute less than 10% of anthropogenic emissions, some of them offer an easy target for sequestration. Figure 2 shows an extensive emission field of CO2-bubbles from the shallow seafloor near the Greek island of Milos (12). It is known that these gases are guite hot until they come very close to the surface. Once in the sea water the bubbles assume of course the temperature of the water, but if one digs into the beach sand with bare hands, one must stop at 30 cm depth in order not to burn the hands. If one would cover an active emission area with olivine sand to slightly above sea level, the CO2 wouldn't lose its temperature as long as it is still isolated by the surrounding olivine grains. It is well-known that silicates are excellent isolators, so the temperature within the olivine pile will rise. This results in rapid weathering of the olivine in the pile, raising the temperature even further on account of the large heat of reaction. The olivine weathers even faster in saline waters than in fresh waters. Conceivably this will set a convection system into motion, in which the hot interstitial water is rising to the top of the olivine island, drawing cold seawater in from the sides into the pile. If a small pool is excavated on top of the island, this will be heated by the rising hot water. This can become an exciting ecotouristic outing, permitting people to bathe in the winter in a warm pool on top of a small Greek island surrounded by a chilly sea, and knowing that this all helps to counteract climate change.

Another example comes also from Greece. In Northeastern Greece there are a number of geothermal wells that emit large CO2 streams. By constructing piles of crushed olivine over these wells, the hot water/CO2 mixtures will start to react with the olivine, which adds the heat of reaction to the total heat production of the system. This may be applied for example for space heating of greenhouses, thus giving an interesting twist to the term greenhouse gas.

The third example is from Lake Nyos in Cameroon (20). The lake, which is of volcanic origin, has an ominous reputation. In 1986 a cloud of CO2 rose from the lake bottom and rolled down the slopes of the mountain, killing more than 1700 people. In order to prevent a repetition of this disaster, a kind of geyser-like system has been installed which lifts the bottom waters (21). When the pressure diminishes, bubbles of CO₂ nucleate and bubble upward, thus preventing the accumulation of this greenhouse gas in the bottom waters by continuously removing it. The system works, but is energy-intensive and expensive, and besides, the CO2 is not captured but emitted towards the atmosphere. It is proposed instead to cover the lake bottom with olivine sand (22) The slowly accumulating CO2 will react with the olivine, transforming it into bicarbonate. The dissolution of olivine in the lake water will make this water slightly alkaline, transforming part of the CO2 into dissolved bicarbonate. Theoretically the heat of reaction might heat up the bottom waters sufficiently to set a gentle convection system in motion. When these waters rise, their pressure will diminish and any remaining CO2 will exsolve and gently and continuously escape to the atmosphere.

CO2 sequestration from natural sources cannot on its own solve the greenhouse problem, but it can contribute to the solution. It should also underline the lesson, that sequestration of CO2 can be done anywhere in the world, independent of origin or location. It does not need to be limited to industrially produced CO2. If the sequestration can serve at the same time some additional beneficial purposes (ecotourism, production of green energy, safety) so much the better. Negative environmental effects are not expected, because olivine weathering is going on in