CO2 capture technologies

Enhanced weathering of olivine as a cheap and sustainable CO2 capture strategy

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Introduction
This proposal deals with an innovative way to combat climate change by the use of olivine to capture CO2. Climate change is caused by the rising CO2 concentrations in the atmosphere, and is a problem that concerns every inhabitant of the earth. Olivine is a magnesium-silicate with an admixture of iron. Olivine has an average composition around (Mg0.92Fe0.08)2SiO4, and is the most common silicate in the world, because it makes up most of the Earth’s mantle. It occurs also at or near the Earth’s surface, where it is found in many places as huge massifs. These massifs are slabs that have been pushed up from the mantle during the processes of mountain building. Every continent has a large number of such massifs of olivine-rich rocks, sometimes covering hundreds of square kilometers and with thicknesses of several kilometers. Olivine is mined, mainly for the steel industry, in a number of locations. In Europe, for example, olivine mines are found in the Ural, in Greenland, Norway, Spain, Italy, Austria and Turkey, and large massifs of olivine-rich rocks occur in Finland, Sweden, the Balkan countries, Greece and Cyprus as well.

The mineral is unstable at low temperatures in the presence of CO2 and water. This means that it weathers easily, and sequesters CO2 in the process. This process is called chemical weathering, and we propose to use this process to reduce the high CO2 levels of the atmosphere, which are believed to cause climate change. By spreading powdered olivine on land or in shallow seas, large volumes of CO2 can be sequestered. It is expected to make a large and sustainable contribution to the problem. It will be considerably less expensive than current proposals to sequester CO2.

What determines the CO2-concentration in the atmosphere?
The total amount of CO2 in the system atmosphere/biosphere/hydrosphere can only change if CO2 is added to it (input) or subtracted from it (output). The input comes mainly from the mantle, among others by volcanoes. The output is mainly by chemical weathering, which changes CO2 into bicarbonate. A modest part of the output is the organic carbon that is stored in geological formations. The bicarbonate solutions produce carbonate sediments in the oceans (limestones, which consist mainly of CaCO3, and dolomites that consist of CaCO3.MgCO3). In pre-industrial times the input from degassing of the mantle was roughly balanced by the output by chemical weathering followed by carbonate precipitation. This balance kept the CO2 concentration of the atmosphere more or less constant.

Since the industrial revolution, the burning of fossil fuels is causing a rapid rise of the atmospheric CO2 levels, because the process of chemical weathering cannot keep pace with this rapidly increasing input. Chemical weathering is a surface process, and runs slowly in the case of solid rocks. We can speed it up by crushing the rock, and spread the
resulting olivine powder over land (Schuiling & Krijgsman, 2006 b). A neat way of doing this is by pre-mixing the olivine with fertilizer before spreading.

**How does chemical weathering work?**

Chemical weathering can be briefly described as the neutralization of an acid by rocks. Dissolved CO\(_2\) is a weak acid. Rocks are mixtures of minerals, and each mineral species has its own specific properties. Some minerals react quickly (geologically speaking!) with CO\(_2\) and water, and dissolve or are transformed into new minerals. Other more resistant minerals survive the weathering process, and are transported as sand grains.

When we consider the fate of olivine during weathering, we can distinguish two cases, namely its behavior in a more or less closed system or in an open system. In an open system like a soil, the rainwater enters the soil, reacts with it and trickles down, and is replaced by a new batch of rain water. A closed system, for example, is an autoclave, where the fluid remains inside and is not replaced by a new batch of fluid. The resulting reactions are quite different.

In closed systems the reaction produces two solids, serpentine and magnesite:

\[
2 \text{Mg}_2\text{SiO}_4 + \text{CO}_2 + 2 \text{H}_2\text{O} \rightarrow \text{Mg}_3\text{Si}_2\text{O}_5(\text{OH})_4 + \text{MgCO}_3
\]

(1)

| olivine | serpentine | magnesite |

In open systems, where the reacting fluids flow through the system, and are constantly replenished, like during weathering, the reaction becomes:

\[
2 \text{Mg}_2\text{SiO}_4 + 8 \text{CO}_2 + 8 \text{H}_2\text{O} \rightarrow 2 \text{Mg}^{2+} + 8 \text{HCO}_3^- + 2 \text{H}_4\text{SiO}_4^0
\]

(2)

It is important to note that during weathering, the same amount of olivine will sequester 8 times as much CO\(_2\) as in a closed system, like an industrial autoclave.

Reaction (2) is the reaction that happens when olivine weathers, and we have proved this conclusively by sampling a number of spring waters in olivine-rich rocks in Turkey. We can distinguish the following steps in the formation of these spring waters.

1. Rainwater, slightly acid because of dissolved CO\(_2\) from the air, falls on the ground.
2. It penetrates the soil, and equilibrates with the soil atmosphere. The soil atmosphere is always much richer in CO\(_2\) than the open air, because creatures that live in the soil are breathing and dead plant material is decaying, all producing CO\(_2\).
3. This water, enriched in CO\(_2\) and thereby acidified and reactive, infiltrates the rock, and starts to attack it. The soil solution is neutralized by the rock (meaning that dissolved CO\(_2\) changes into bicarbonate ions) and the rock releases its cations, mainly Mg\(^{2+}\), and usually some Ca\(^{2+}\) as well.
4. Thereafter these waters, which are no longer reactive, slowly trickle downward through the rock, and emerge as springs. These spring waters have a pH between 7.6 and 8.8.
Figure 1 shows the composition of these waters. It confirms the reaction as given above and demonstrates the very close relation between the amount of Ca + Mg released from the rock and the amount of CO$_2$ that is sequestered in the process. It also provides us with data on the amount of CO$_2$ that is annually sequestered by a single massif of olivine-rich rocks. As can be seen in the figure, each liter of rainwater or snow melt that penetrates into the soil takes up on average 350 mg of CO$_2$.

How can we use this to combat climate change?
Because the man-made production of CO$_2$ is 15 to 20 times larger than the natural input into the system hydrosphere/atmosphere/biosphere, we must speed up the rate of chemical reaction by the same factor to restore the balance. How can we do that?
Chemical reaction (2) shows that we need to mine approximately 7 km$^3$ of olivine each year to sequester all the CO$_2$ that was emitted by mankind in that same year. Can this be done? In order to understand the size of the problem it is good to have some numbers for comparison. Olivine mines will certainly be open pit mines. The biggest open pit mines in the world have volumes around 20 km$^3$. The volume of cement poured each year is about 6 km$^3$. For its production a similar volume of carbonate rocks is mined. So one can conclude, the required scale of olivine mining of 7 km$^3$ per year is large, but within the range of normal mining operations, certainly if olivine mining will be distributed over several tens of olivine mines, all over the world, which will reduce transport costs. Existing olivine mines should increase their production, and new olivine mines should be started.
One should mine the olivine, and grind it to the required size (below 100 micron). Grinding of rocks is a standard operation in mining, and ball mills or vertical mills (roller mills) can be found at every mine. The cost of grinding to 100 micron is about 1.65 Euro/ton, and a large part of that fraction consists, of course, of particles that are smaller...
than 100 micron. Under favorable conditions, these will weather (and sequester CO\textsubscript{2}) in a few years. These conditions are:

- A temperature around 25-30\textdegree C (tropical climate)
- A grain size of 100 micron or less
- A starting pH around 5 or slightly less, like in most soils
- The presence of organic acids (humic or fulvic acids)
- The presence of at least a few % of the fayalite molecule (Fe\textsubscript{2}SiO\textsubscript{4}) in the olivine.

Olsen and Rimstidt (2007) give a diagram on the lifetime of olivine grains. From this diagram under the conditions given above we can see that the predicted lifetime is in the order of 10 years. It should be understood that the process starts right after spreading.

**How should we proceed?**

A number of new olivine mines should be started in humid tropical countries (Central and South America, Central and West Africa, South-East Asia). The olivine is ground at location and then spread in the (wider) surroundings of these mines. This way we combine the following advantages:

- Chemical weathering under favorable warm and humid conditions
- Low wages.
- New employment opportunities in developing countries
- Limited transport and handling costs

The cost of crushed olivine on board ship in the port of destination is now around 23 Euro per ton. When new olivine mines are opened in low-wage countries, and the size of the mining operations increases, giving an economy of scale, and when transport costs are limited, it is expected that the price will go down to 10 to 15 Euro/ton.

A first contact has been established in Guinea, where at our request the Geological Survey is exploring the possibility of olivine mining on the Kaloum Peninsula, near the capital Conakry.

**Is it new and innovative?**

We were probably the first to use olivine for the neutralization of waste acids in the eighties (Schuiling, v.Herk and Pietersen, 1986), but nowadays a number of research groups, mainly in the USA and Canada, but also in several European countries are working on technologies to sequester CO\textsubscript{2} by reacting it with olivine, sometimes with partial success. Other popular approaches are the capture and underground disposal of CO\textsubscript{2} from the stack gases of power plants. Both approaches suffer from misconceptions.

**Misconception 1**

_We need a technology. In companies this means that their scientists are asked to develop a technology._

**Answer:** We don’t. If nature can perform the same task, there is no need to develop expensive and energy-intensive new technologies.
Misconception 2
We must capture the CO$_2$ emitted by power plants.
Answer: We don’t. One CO$_2$ molecule is as good as the other, so if capturing the CO$_2$ from the atmosphere is cheaper, there is no need to capture the emissions of power plants.

Using olivine to sequester CO$_2$ is not an invention, but a novel concept based on geochemical engineering (Schuiling, 1998). What is new is the concept of how to apply it, not by a new technology, but by invoking the help of nature. This involves a radical change in our way of thinking. Instead of relying on technologies, we use a natural process that is going on already for 4.6 billion years. What we add is several ways to speed it up by grinding it and spreading, and selecting the most favorable climate where it may proceed fastest, and the best economical conditions.

Most people tend to believe that man-made technologies are more trustworthy than nature, despite evidence to the contrary. Human errors, and our inability to understand the complex interactions between the technology and the natural conditions often result in failure. But even in case the technology would work, and one has a choice between a new technology and a natural process, it is usually better to choose the natural process for economical reasons. For global problems like climate change, one should realize that global problems require global solutions, and no high-tech fixes.

Should the application be limited to tropical developing countries?
There are several good reasons to extend the application to industrialized nations in temperate climates as well. Many soils, and many lakes in temperate climates are acid, and their quality would improve if the pH is raised. This is routinely done on a large scale by liming. Liming is the spreading of powdered CaCO$_3$ over the soil or over a lake. It is essentially greenhouse gas neutral. The calcium carbonate first dissolves, and then is transported to the oceans, where it will precipitate again after some time as calcium carbonate, without a net sequestration of CO$_2$. If liming would be replaced by the spreading of olivine, it has the same positive effect on pH buffering, but it leads to a net sequestration of CO$_2$ at the same time. In terms of cost involved, the two operations are comparable. Another benefit is that the olivine acts as a slow-release source of magnesium, thereby saving on fertilizer costs.

There is, in my opinion, not only a technical, but also an ideological argument in favor of olivine spreading in developed nations as well. If one can buy small bags of olivine powder in supermarkets, gardening centers or gas stations, many people will become involved and committed. Each individual contribution is small, but everybody can feel that he has personally taken part in the fight to combat climate change, if he spreads his bag of olivine powder over his own lawn.
Moreover, by letting the industrialized nations do their own share, the developing nations will not get the uneasy feeling that they are the ones to be saddled with our problems. Our energy-intensive industries as well as our fuel consumption should be taxed in order to pay for the olivine mining, milling, spreading and monitoring in tropical countries. A rough calculation shows that a worldwide carbon tax of 5 cents per liter of fuel will amply cover these costs.
What could a project involve?

The ramifications are endless. A number of possibilities are the following:

- determination of the rate of weathering of olivine grains of different grain sizes in different soils and different climates.
- monitoring of the effect of olivine spreading on CO₂ sequestration by means of monitoring boreholes, where samples of ground water will be taken. These ground waters will be analyzed for changes in pH, bicarbonate and magnesium.
- establishing contacts with parties (e.g. geological surveys) in developing countries, to explore their potential for olivine mining.
- finding the right approach to involve the general public in the campaign to combat climate change by making use of natural weathering of olivine.
- in addition we have enumerated in the next paragraph a number of niche applications for olivine, which will all lead, directly or after some time to CO₂-sequestration. Several of these applications have sprung from my discussions with large companies that have shown an interest to introduce the use of olivine into their activities.

In each of these issues professional help from Altran consultants would be of great assistance.

Niche applications

Apart from the main application, olivine could also be used for a number of special applications which can all help to combat climate change as well. Olivine has a comparable hardness as quartz, so obvious applications are in the replacement of quartz sand by olivine. We will enumerate but a few, but the ramifications are numerous.

- Olivine is already replacing quartz sand in sandblasting, to avoid the danger of silicosis by fine-grained freshly broken quartz dust. Governments could speed up this transition to olivine by subsidizing its use.
- Quartz sand is incorporated in the top layers of highways. Olivine has practically identical mechanical properties. Traffic will slowly wear away the grains, and the resulting olivine dust particles will fall on the surroundings and start to sequester CO₂.
- Olivine can be added to sound walls along highways which should preferably be covered by vegetation. Weathering of the olivine will sequester CO₂, thus “greening” the highways.
- The possibilities to replace quartz sand by olivine in cement and other construction materials should be investigated. Although during the lifetime of the constructions the mechanical properties of olivine will dominate, after the demolition of the buildings it will start to play its role in sequestering CO₂.
- Quartz sand is often supplied to reinforce coasts that are vulnerable for erosion. A case in point is the “Hondsbossche Zeewering”, a weak spot along the Dutch coast. Another opportunity could be the renovation of the “Afsluitdijk”. By adding olivine sand directly from ships, which is considerably less expensive than unloading and handling in ports, at least an equal level of protection can be achieved. Olivine grains of 1 mm will last hundreds of years. Because olivine is heavier than quartz (S.G.3.3 versus 2.6), it will less easily be washed away by
storms or currents. When the grains are moving and rubbing against each other, some of the material will be chipped off. These fine particles will rapidly react with seawater. The added alkalinity protects the sea from acidification and increases its capacity for CO$_2$ uptake.

- In experiments carried out by our group in the eighties, it was found that fine-grained olivine in a fixed bed in a closed system was cementing itself. In analogy, one could check in marine systems whether it is possible to construct reefs by depositing large heaps of olivine sand in shallow seas, and let it slowly react with the interstitial seawater. It is well possible that the increase in pH of the included pore water will lead to the crystallization of CaCO$_3$ which will cement the grains and thus form a solid reef.

- Salt is mined from evaporite deposits by solution mining. This leaves large underground cavities. In order to avoid the collapse of such cavities, leading to subsidence at the surface, measures must be taken to counteract it. In several Dutch cases, at a depth around 400 meters, this means that the cavities must remain filled with saturated brine under pressure. If instead, these cavities are filled with fine-grained olivine, the replaced brine can be recovered, and the olivine will react with the remaining interstitial brine. By injecting also some CO$_2$, reaction (1) will proceed. The average temperature downhole at 400 meter depth will be around 23 degrees compared to ~11 degrees at the surface. This will speed up the reaction. Because the volume of the serpentine + Mg-carbonate that is formed is larger than that of the olivine in the starting material, the pores between the grains are closed, and a solid rock is formed inside the cavity. This will eliminate the need for constant pressurizing and monitoring of these cavities. There is even the possibility to recover part of the heat of reaction, because the surrounding rocks are excellent thermal isolators (Schuiling, 1964 and 2006 a). This will prevent the heat, produced by the reaction, to leak away before it can be recovered.
**Outline of a Project**

*Which subjects could be further developed with the aid of Altran? (note: this is not an exhaustive list)*

**Technical problems**
- Rates of reaction of olivine grains as a function of climate, grain size and pH under natural conditions.
- Does it make a difference if the olivine grains are spread over the surface, or plowed under.
- How can the effects of olivine spreading on land and along coasts be monitored.
- How do olivine grains behave in marine constructions.
- Use of olivine suspensions for backfilling of cavities caused by solution mining.
- Selection of sites in tropical developing countries where olivine mines could be started.

**Socio-economical problems**
- What are effective means to (further) involve the general public to take an active part in combating climate change.
- What are the benefits and possible drawbacks of starting a number of olivine operations in tropical developing countries.

**Legal (regulatory) problems**
- How can development aid be used, to the benefit of the receiving countries as well as the donor countries, to develop olivine mining, and spreading of the crushed olivine in tropical countries.
- How can governments promote/impose the use of olivine instead of quartz sand in sandblasting operations.
- What measures can be taken to realize the change from the liming of acid soils or acid lakes to olivine spreading.
References