

Synopsis of paper on mineral carbonation in peridotite for CO<sub>2</sub> capture and storage (CCS),  
by Peter Kelemen and Jürg Matter in Proceedings of the National Academy of Sciences, 2008,  
in the context of other CCS techniques

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By speeding up natural processes, scientists hope that rocks from the Earth's deep interior, exposed on the surface by plate tectonics and erosion, may be able to capture and store billions of tons of CO<sub>2</sub> per year. Compare this to the total human output of CO<sub>2</sub> to the atmosphere, currently about 30 billion tons of CO<sub>2</sub> per year, and you can see that this could make a significant difference in the overall CO<sub>2</sub> budget of the planet until alternative energy sources replace global fossil fuel use. Given concern about CO<sub>2</sub>-driven global warming and ocean acidification, CO<sub>2</sub> capture and storage ideas are receiving increasing attention.

Since 1990, scientists and engineers have considered using naturally occurring minerals that react with CO<sub>2</sub> to form different, carbonate minerals, as a means to capture CO<sub>2</sub> from the atmosphere and store it in solid form where it will remain stable and inert for thousands or millions of years (*Seifritz, Nature 1990*). Since then, the mineral olivine (Mg<sub>2</sub>SiO<sub>4</sub>) has been the focus of the most research. Olivine forms the carbonate mineral magnesite via reactions such as



Because olivine is abundant, has more magnesium than silicon, and reacts readily because it is far from equilibrium with the atmosphere and surface waters, olivine is particularly efficient for this kind of reaction.

Olivine forms 60 to 80% of the Earth's upper mantle, which in turn comprises about ¼ of the Earth. However, mantle rocks are ordinarily shielded from reaction with the atmosphere and surface waters by a shell of continental crust, 40 km thick, or oceanic crust 7 km thick. Collisions of tectonic plates cause mantle rocks to be thrust onto the continents, where they are later exposed by erosion in mountain belts. The world's largest exposures of olivine-rich mantle rocks are in the Sultanate of Oman, New Caledonia (Nouvelle Calédonie), Papua New Guinea, and the Baltic countries. In North America, some large deposits occur in northern California, southern Oregon, Montana and eastern Canada.

Initially, engineers focused on using olivine to capture and store CO<sub>2</sub> via “*ex situ*” methods. Olivine-rich rocks were to be quarried, transported to power plants, ground to a fine powder, and mixed with water plus purified CO<sub>2</sub> in reaction vessels at high pressure and temperature. These methods for olivine carbonation “at the smokestack” have proved to be relatively expensive, in both financial and energy terms, though engineers continue to seek methods to improve their efficiency (*Mazzotti et al., Chapter 7, in Metz et al., IPCC Special Report on Carbon Dioxide Capture and Storage, 2005*). Meanwhile, most proposed CO<sub>2</sub> capture and storage methods rely on injection of pure CO<sub>2</sub> in dense, supercritical liquid form into pore space in sub-surface rocks, or even into “puddles” of dense CO<sub>2</sub> on the seafloor. There, scientists hope, the supercritical CO<sub>2</sub> will stay.

There is an incentive to look for alternatives, since storage of CO<sub>2</sub> in inert, solid carbonate minerals could be safer, and easier to monitor and verify, than storage of CO<sub>2</sub> liquid in pore space. Thus, over the past decade some scientists have focused on “*in situ*” mineral carbonation, leaving rocks in the ground and using methods such as injection of CO<sub>2</sub> to increase reaction rates. Much of this work has been on carbonation of an abundant type of lava, basalt, which contains minor amounts of olivine together with large proportions of alumino-silicate minerals such as plagioclase feldspar. Basalt carbonation is slower than carbonation of olivine, but basalt is abundant near many large power plants (*e.g., Goldberg et al Proc. Nat. Acad. Sci. 2008*). The idea is to pump CO<sub>2</sub> into pore space in basaltic lava, with the expectation that over decades the CO<sub>2</sub> will combine with olivine and feldspar to produce solid carbonate minerals

Recently, Peter Kelemen and Jürg Matter, at Columbia University's Lamont Doherty Earth Observatory, turned their attention to *in situ* carbonation of mantle rocks rich in olivine (*Kelemen & Matter, Proc. Nat. Acad. Sci. 2008*). They've made two key observations. First, natural carbonation of

olivine proceeds much more rapidly than geologists had previously guessed. In Oman, their samples of solid carbonate terraces (“travertine”) forming from spring water emanating from mantle rocks, and of carbonate veins that formed within mantle rocks beneath the surface and were later exposed by erosion, have an average  $^{14}\text{C}$  age of about 25 *thousand* years, whereas scientists in the past guessed that the veins were 95 to 40 *million* years old.

Second, Kelemen and Matter found that the olivine carbonation process can be “self-heating”. Carbonation of olivine gives off heat energy – basically because it involves condensation of  $\text{CO}_2$  gas or liquid to form  $\text{CO}_2$ -bearing solids. If the carbonation reaction is fast enough, the heat evolved can offset cooling due to diffusion from hot rocks into their cold surroundings, and due to flow of cold fluid through the rocks. At elevated pressure, perhaps one kilometer below the Earth’s surface, the carbonation reaction goes fastest at about  $185^\circ\text{C}$ . Under such conditions, the rock volume could become “self-heating”: Kelemen and Matter calculated that cold  $\text{CO}_2$ -bearing fluid can be pumped into the rocks at about 4 centimeters per second without cooling the rocks and slowing the reaction. Thus, they propose that one method of speeding up olivine carbonation would be to “jump start” the process by drilling, fracturing, and heating a rock volume at depth to about  $185^\circ\text{C}$ , and then pumping purified  $\text{CO}_2$  plus water into that rock volume. They calculate that such a process would convert billions of tons of  $\text{CO}_2$  into solid carbonate minerals per cubic kilometer of rock per year.

Such an *in situ* process might be less expensive than *ex situ* olivine carbonation, “at the smokestack”, for several reasons. First, it avoids the cost of quarrying, transporting and grinding rock reactants. Once a rock volume is heated, the energy to sustain high temperature at depth would be provided by the carbonation reaction itself. Sustained pressure would be provided, to some extent, by the presence of overlying rocks. However, the cost of most  $\text{CO}_2$  capture and storage methods is dominated by the process of  $\text{CO}_2$  capture at power plants, and this proposal is no exception. Further, a truly globally important process of this type would involve transportation of really large amounts of  $\text{CO}_2$ , comparable to the amounts of oil, gas and coal currently being consumed.

Thus, Kelemen and Matter are beginning to consider an alternative possibility. In its pure end-member, it goes like this. Perhaps shallow seawater, rather than purified  $\text{CO}_2$ , could be used as a fluid to transport  $\text{CO}_2$  into a volume of mantle rocks at depth. Shallow seawater maintains  $\text{CO}_2$  exchange equilibrium with the atmosphere, so this would avoid the costs of industrial  $\text{CO}_2$  capture and transport. As one goes deeper in the Earth, the rocks get hotter, so perhaps one could simply drill into rocks at about  $185^\circ\text{C}$ , rather than pre-heating a rock volume. Pumping might not be needed, since thermal convection might drive cold water to circulate down one hole, following hot water emerging from another. This end-member process using seawater would be thousands of times less efficient, in terms of kilograms of olivine transformed to solid carbonate per cubic kilometer of rock per year, than one using purified  $\text{CO}_2$ . However, in addition to  $\text{CO}_2$  capture and transport, it avoids the costs of pre-heating a rock volume, and pumping fluid at high pressure. If drilling holes and fracturing rocks at depth is thousands of times less expensive than  $\text{CO}_2$  capture and transport, then this end-member idea could be useful. Certainly, this epitomizes the Kelemen and Matter’s philosophy: Understand the processes of natural olivine carbonation, and then do something – as little as possible – to accelerate these processes, inducing them to consume globally significant quantities of atmospheric  $\text{CO}_2$ .