

***In Situ* Mineral Carbonation in Peridotite for CO₂ Capture and Storage**

Peter Kelemen (peterk@LDEO.columbia.edu) and Jürg Matter (jmatter@LDEO.columbia.edu)
Lamont Doherty Earth Observatory, Columbia University

***In situ* reaction of CO₂ with a common rock type, mantle peridotite, to form solid carbonate minerals could be used to capture and store billions of tons of CO₂ per km³ of rock per year ¹. There may be positive feedback regimes in which high reaction rates at high temperature are sustained by exothermic heating, and permeability and reactive surface area are maintained or enhanced by cracking in response to large increases in the solid volume. If these regimes can be accessed, *in situ* peridotite carbonation offers a rapid, relatively inexpensive, and essentially permanent method for CO₂ capture and storage.**

- Natural peridotite carbonation is rapid: CO₂ uptake by near surface carbonation of mantle peridotite during weathering consumes ~ 10³ tons per km³ per year in Oman ¹, and mineral carbonation is up to ~ 10⁶ times faster at 185°C and 100's of bars P_{CO₂} (e.g., ^{2,3}).
- Proposed method (patent pending) ¹, for enhanced, natural carbonation of peridotite *in situ*: (1) Drill peridotite beneath impermeable cap rock, (2) hydrofracture the peridotite, (3) heat rock volume to ~ 185°C at depth using hot H₂O, hot CO₂, flue gas, ..., (4) pump CO₂, or H₂O equilibrated with CO₂, at 100-300 bars P_{CO₂}. Alternatively, use surface water saturated in atmospheric P_{CO₂}, slower but potentially much less expensive.
- Rapid carbonation is self-heating: Peridotite carbonation is exothermic, and this can be used to reduce energy costs via reactive “self-heating”: For example, once a peridotite volume is above ~ 125°C, the reaction rate is fast enough for heat production to exceed diffusive heat loss to cold surroundings and advective heat loss to cold CO₂-rich fluid pumped at ~ 1 cm/s.
- Rapid carbonation may be self-cracking: Though reactions involving crystallization in pore space could be self-limiting due to armoring of reactive surfaces and dropping permeability ⁴⁻¹², extensive outcrops of completely carbonated peridotite (listwanite) show that natural carbonation is not always self-limiting. Listwanites have brecciated textures in outcrop and dense, hierarchical fracture networks extending to microscopic scales, filled by syn-kinematic carbonate and quartz veins, probably due to feedback between volume change, stress increase, and fracturing that maintains permeability and reactive surface area ¹. Hydrothermal systems producing carbonate from peridotite remain active for tens of thousands of years ^{1,13}. Experiments on carbonation of porous peridotite showed increasing permeability vs time ¹⁴.
- Energy cost compared to “simple” injection of CO₂ into subsurface pore space is (a) hydrofracture cost – one time only, probably negligible per ton of CO₂ consumed – and (b) preheating. To heat 100°C with heat capacity 850 J/kgK requires 85 kJ/kg peridotite. Since complete carbonation involves 0.6 kg CO₂/kg peridotite, this is ~ 140 kJ/kg CO₂ consumed. If heating + carbonation is 20% efficient, this requires ~ 700 kJ/kg. Burning fossil fuel to generate electricity produces 3000 to 8000 kJ/kg CO₂. In this case, the energy penalty compared to “simple” injection is ~ 9 to 23%.
- Using surface water (e.g., surface ocean water equilibrated with atmospheric CO₂) as a fluid reactant avoids the cost of CO₂ capture at the source of emission and the cost of CO₂ transport from source to storage site. This is similar to direct “air capture”. Reaction rate is predicted to be ~ 50 times slower at 185°C and 300 bars for P_{CO₂} = 0.0004 P_{total} vs P_{CO₂} = P_{total} ¹.

Since 1990, tectonically exposed peridotite from the Earth's upper mantle, composed mainly of the mineral olivine, has been considered a promising reactant for conversion of atmospheric CO₂ to solid carbonate^{15,16}. Mantle peridotite is ordinarily beneath the Earth's crust, more than 6 km below the seafloor and 40 km below the land surface. It is far from equilibrium with air and water at the Earth's surface. Its exposure via thrust faults along tectonic plate boundaries creates an accessible reservoir of chemical potential energy. However, engineered techniques for *ex situ* mineral carbonation, "at the smokestack", are problematic. Kinetics are slow unless olivine is ground to powder, heat-treated, and held at elevated pressure and temperature (e.g.,^{2,17}). Currently, when combined with the cost of CO₂ capture from flue gas, this involves a 60-180% energy penalty compared to power plants without CCS, and is considered problematic though engineering studies continue¹⁸.

It may be more practical to carbonate peridotite *in situ*, eliminating quarrying, transportation, and grinding, and capitalizing on thick peridotite massifs to reduce diffusive heat loss and maintain fluid pressure¹. Fyfe¹⁹ proposed that exothermic hydration of olivine to form the mineral serpentine may heat peridotite. "Self-heating" is more efficient via carbonation rather than hydration because reaction rates are faster and carbonation enthalpy per kg is larger than hydration¹. Once a rock volume is in the self-heating regime at depth, CO₂-rich fluid entering the volume at surface temperature is heated by the exothermic reaction. Inflow rate can be adjusted to maintain high temperature and optimal peridotite carbonation rates¹. This avoids the cost of maintaining high temperature in a reaction vessel.

Fluid-rock reactions that increase the solid volume are often self-limiting because they fill porosity, reduce permeability, and create "reaction rims" that act as diffusive boundary layers between unreacted mineral reactants and fluid⁴⁻¹². However, crystallization in pore space can also fracture rocks and increase permeability, especially for salts crystallizing from water in limestone and other building materials^{20,21} and the similar process of frost cracking²². MacDonald & Fyfe²³ proposed that increasing solid volume associated with olivine hydration (serpentinization) produces stresses that fracture surrounding rock, as further investigated for serpentinization (e.g.,^{24,25-28}) and granite weathering²⁹. If a rock volume enters this self-cracking regime, this avoids the cost of repeated hydrofracture for *in situ* carbonation, and the cost of grinding solid reactants for *ex situ* carbonation.

Compared to injection of supercritical CO₂ into underground pore space, the added costs for *in situ* peridotite carbonation (preheating and/or hydrofracturing a rock volume at depth) could be small, particularly if the procedure is done in an area with high heat flow where subsurface peridotite is already hot, and thermal convection can drive fluid circulation. Furthermore, if surface water saturated in atmospheric P_{CO2} is used as a fluid reactant, the proposed process can be used for "negative CO₂ emissions", similar to air capture and unlike CO₂ capture at power plants and other sources. However, the rate enhancement due to temperature and pressure is ~ 50 to 100 times smaller if sea water rather than CO₂-rich fluid is used as a reactant, and the rate of exothermic heating is correspondingly reduced¹.

Together with gathering background information on fracture density, porosity and permeability in tectonically exposed peridotite massifs, the controls on permeability evolution during peridotite carbonation represent the most crucial avenue for future research on this topic. This research is worthwhile because of the potential for permanent storage of immense amounts of CO₂. In Oman, a thrust sheet of oceanic crust and upper mantle known as the "Oman ophiolite" is ~ 70,000 km³³⁰. ~ 30% of this volume is peridotite. Adding 1 wt% CO₂ to this peridotite would consume ¼ of all atmospheric CO₂. Full carbonation of peridotite, forming solid carbonates + quartz, would consume more than 40 wt% CO₂, corresponding to almost 30,000 Gt of CO₂ in the Oman peridotite alone. Similar size ophiolites are in Papua New Guinea (outcrop ~ 10,000 km²), New Caledonia (~ 6000 km²) and along the east coast of the Adriatic Sea (several ~ 4000 km² massifs). In the US, the largest bodies of peridotite include the base of the Stillwater intrusion in southern Montana, and the Trinity peridotite near Mt Shasta volcano in northern California. Parts of the Trinity peridotite, and smaller peridotite bodies in the Geysers area of Sonoma County, California, have been heated to more than 100°C within a few kilometers of the surface.

1. Kelemen, P. B. & Matter, J. M. In situ carbonation of peridotite for CO₂ storage. *Proc. Nat. Acad. Sci. USA* 105, 17,295-17,300 (2008).
2. O'Connor, W. K., Dahlin, D. C., Rush, G. E., Gerdemann, S. J. & Nilsen, D. N. 21 pages plus appendices (Office of Process Development, Albany Research Center, Office of Fossil Energy, US DOE, Albany, OR, 2004).
3. Béarat, H. et al. Carbon sequestration via aqueous olivine mineral carbonation: Role of passivating layer formation. *Environ. Sci. Technol.* 40, 4802-4808 (2006).
4. Tenthorey, E., Scholz, C., Aharonov, E. & A, L. Precipitation sealing and diagenesis - 1. Experimental results. *J. Geophys. Res.* 103, 23,951-23,967 (1998).
5. Aharonov, E. Precipitation sealing and diagenesis - 2. Theoretical analysis. *J. Geophys. Res.* 103, 23,969 (1998).
6. Milsch, H., Seibt, A. & Spangenberg, E. Long-term Petrophysical Investigations on Geothermal Reservoir Rocks at Simulated In Situ Conditions. *Transport in Porous Media* 77, 59-78 (2009).
7. Morrow, C., Moore, D. & Lockner, D. Permeability reduction in granite under hydrothermal conditions. *J. Geophys. Res.* 106, 30,551-30,560 (2001).
8. Cipolli, F., Gambardella, B., Marini, L., Ottonello, G. & Zuccolini, M. V. Geochemistry of high-pH waters from serpentinites of the Gruppo di Voltri (Genova, Italy) and reaction path modeling of CO₂ sequestration in serpentinite aquifers. *Applied Geochem.* 19, 787-802 (2004).
9. Lowell, R. P. & Rona, P. A. Seafloor hydrothermal systems driven by the serpentinization of peridotite. *Geophys. Res. Lett.* 29, 1531, doi 10.1029/2001GL014411 (2002).
10. Martin, B. & Fyfe, W. S. Some experimental and theoretical observations on kinetics of hydration reactions with particular reference to serpentinization. *Chem. Geol.* 6, 185-202 (1970).
11. Emmanuel, S. & Berkowitz, B. Suppression and stimulation of seafloor hydrothermal convection by exothermic mineral hydration. *Earth Planet. Sci. Lett.* 243, 657-668 (2006).
12. Xu, W. Y. & Pruess, K. Numerical simulation of CO₂ disposal by mineral trapping in deep aquifers. *Applied Geochem.* 19, 917-936 (2004).
13. Früh-Green, G. L. et al. 30,000 years of hydrothermal activity at the Lost City vent field. *Science* 301, 495-498 (2003).
14. Andreani, M. et al. Experimental study of carbon sequestration reactions controlled by the percolation of CO₂-rich brine through peridotites. *Environ. Sci. Technol.* 43, 1226-1231 (2009).
15. Lackner, K. S., Wendt, C. H., Butt, D. P., Joyce, E. L. & Sharp, D. H. Carbon dioxide disposal in carbonate minerals. *Energy* 20, 1153-1170 (1995).
16. Seifritz, W. CO₂ disposal by means of silicates. *Nature* 345, 486 (1990).
17. Lackner, K. S., Butt, D. P. & Wendt, C. H. Progress on binding CO₂ in mineral substrates. *Energy Conversion & Management* 38, S259-S264 (1997).
18. Mazzotti, M. et al. in *IPCC Special Report on Carbon Dioxide Capture and Storage* (eds. Metz, B., Davidson, O., de Coninck, H., Loos, M. & Meyer, L.) 319-338 (Cambridge University Press, Cambridge, UK, 2005).
19. Fyfe, W. S. Heats of chemical reactions and submarine heat production. *Geophys. J. Roy. Astr. Soc.* 37, 213-215 (1974).
20. Scherer, G. W. Stress from crystallization of salt. *Cement and Concrete Research* 34, 1613-1624 (2004).
21. Scherer, G. W. Crystallization in pores. *Cement and Concrete Research* 29, 1347-1358 (1999).
22. Walder, J. & Hallet, B. A theoretical model of the fracture of rock during freezing. *Geological Society of America Bulletin* 96, 336-346 (1985).
23. MacDonald, A. H. & Fyfe, W. S. Rate of serpentinization in seafloor environments. *Tectonophysics* 116, 123-135 (1985).
24. Evans, B. W. The serpentinite multisystem revisited: Chrysotile is metastable. *Int. Geol. Rev.* 46, 479-506 (2004).
25. O'Hanley, D. S. Solution to the volume problem in serpentinization. *Geology* 20, 705-708 (1992).
26. Shervais, J. W., Kolesar, P. & Andreasen, K. A field and chemical study of serpentinization, Stonyford, California: Chemical flux and mass balance. *Int. Geol. Rev.* 47, 1-23 (2005).
27. Iyer, K., Jamtveit, B., Mathiesen, J., Malthe-Sorensen, A. & Feder, J. Reaction-assisted hierarchical fracturing during serpentinization. *Earth Planet. Sci. Lett.* 267, 503-516 (2008).
28. Jamtveit, B., Malthe-Sorensen, A. & Kostenko, O. Reaction enhanced permeability during retrogressive metamorphism. *Earth Planet. Sci. Lett.* 267, 620-627 (2008).
29. Fletcher, R. C., Buss, H. L. & Brantley, S. L. A spheroidal weathering model coupling porewater chemistry to soil thickness during steady-state denudation. *Earth Planet. Sci. Lett.* 244, 444-457 (2006).
30. Nicolas, A., Boudier, E., Ildefonse, B. & Ball, E. Accretion of Oman and United Arab Emirates ophiolite: Discussion of a new structural map. *Marine Geophys. Res.* 21, 147-179 (2000).

