

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

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IODP could play an essential role in research on sub-seafloor, geological capture and storage of CO₂. There are numerous advantages to CO₂ capture and storage beneath the seafloor. Thus, IODP offers an ideal platform for this endeavor, leading the worldwide scientific effort in identifying potential sites and in confirming a secure approach for geologic CO₂ sequestration. A variety of mechanisms have been proposed, including (1) *in situ* reaction of CO₂ with peridotite and basalt to form solid carbonate minerals, (2) injection of supercritical CO₂ into pore space in lava flows covered by an impermeable cap rock, and (3) injection of supercritical CO₂ into porous sediments overlain by impermeable cap rock.

Perhaps more importantly, groups are exploring subsea, geological capture of CO₂ via mineral carbonation in basalt and peridotite, in addition to storage. If greenhouse gas concentrations become too high to sustain an acceptable quality of life, “negative emissions” will be necessary. Along with carbon capture from biofuel power plants, enhanced geologic capture of CO₂ from air or shallow seawater can deliver negative emissions. By contrast, CO₂ capture at fossil fuel power plants, at best, can only achieve zero emissions.

We propose that IODP convene a workshop within the coming year to gather research scientists, government officials and industry experts to outline a consensus on research directions, identify existing and planned proposals with potential for CCS synergy, begin to identify specific sites for CCS-focused research drilling, and discuss possible industry-IODP collaboration on CCS research.

IODP research on CO₂ capture and storage (CCS) can be undertaken during expeditions focused mainly on more traditional studies of mantle peridotite, volcanic basalt and sedimentary sections. Conversely, traditional objectives can be pursued on expeditions designed around CCS. CCS-related research can be done at core complexes where peridotites are exhumed to the seafloor, at offshore extensions of ophiolites and peridotite massifs, for example offshore from northern Oman, New Caledonia, Papua New Guinea, eastern Spain (Alboran Sea), and the Balkans, in flood basalt provinces, and in passive margin sedimentary sequences. There is obvious synergy between CCS and biogeochemistry objectives because mineral hydration – associated with mineral carbonation in peridotite – may have provided an energy source for early life, and because mineral carbonation may be enhanced by biological catalysis.

Of particular interest for CCS-related research are characterization of geologic processes of mineral carbonation and hydration, characterization of permeability and existing carbonate alteration in these settings, and hole-to-hole experiments. Ultimately, IODP research could include injection of shallow seawater, and/or CO₂-rich fluid, to test proposed methods for rapid, geologic CCS via mineral carbonation or injection into pore space.

The authors of this particular White Paper specialize in the study of *in situ* mineral carbonation in peridotite and basalt. In order to provide a technical rationale for such research, below we provide an outline of our overall approach. In advocating research effort on peridotite and basalt carbonation, we do not wish to detract in any way from proposed research on injection of CO₂ into permeable sub-seafloor sedimentary formations. We firmly believe that an ensemble of solutions, rather than a single “best” solution, will be required in order to avoid and offset increasing anthropogenic CO₂ emissions to the atmosphere.

Since 1990, tectonically exposed peridotite and basalt, rich in Mg and Ca, have been considered promising reactants for conversion of atmospheric CO₂ to solid carbonate^{1,2}. However, engineered techniques for *ex situ* mineral carbonation, “at the smokestack”, are problematic. Kinetics are slow unless mineral reactants are ground to powder, heat-treated, and held at elevated pressure and temperature (e.g.,^{3,4}) or pre-treated with concentrated acids and then exposed to CO₂ at elevated pressures and temperatures. 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, though engineering studies continue⁵.

Alternatively, *in situ* reaction of CO₂ peridotite to form solid carbonate minerals could be used to capture and store billions of tons of CO₂ per km³ of rock per year using pure CO₂ as a transport fluid⁶. This may be more practical than *ex situ* carbonation, eliminating quarrying, transportation of solid reactants, and grinding, and capitalizing on thick peridotite massifs to reduce diffusive heat loss and maintain fluid pressure. *In situ* mineral carbonation in basalt is likely to be slower than in peridotite⁷, but basalts are more abundant near the Earth’s surface, and have higher permeability^{8,9}. There may be positive feedback regimes in which high reaction rates at high temperature are sustained by exothermic heating, while permeability and reactive surface area are maintained or enhanced by cracking in response to large increases in the solid volume⁶. If so, *in situ* peridotite and basalt carbonation offer a rapid, relatively inexpensive, and essentially permanent method for CO₂ capture and storage. Using 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”. Because seawater cannot be delivered to a reaction site too rapidly, without cooling a rock volume, and the CO₂ concentration in seawater is low, the overall rate of carbonate formation is predicted to be ~ 100 to 1000 times slower at 185°C and 300 bars for $P_{CO_2} = 0.0004 P_{total}$ vs $P_{CO_2} = P_{total}$.

Areas where peridotite or permeable basalt are present within a few km of the seafloor (deep enough to stabilize high density, supercritical CO₂ fluid), in shallow water, overlain by an impermeable sedimentary cap, preferably in areas of high heat flow, form ideal sites for IODP studies of present day alteration, permeability, response to elevated fluid pressure (hydrofracture), and perhaps pilot injections of CO₂.

- **Natural peridotite carbonation is rapid:** CO₂ uptake by near surface carbonation of mantle peridotite during weathering consumes ~ 10³ tons per km³ per year in Oman⁶, and mineral carbonation is up to ~ 10⁶ times faster at 185°C and 100’s of bars P_{CO₂} (e.g.,^{4,10}) yielding potential rates ~ 1 Gt/km³/year. Natural basalt carbonation is probably slower⁷ but, because basalts are very extensive, consumes ~ 10⁸ tons CO₂/year globally¹¹.
- There is a proposed method (patent pending)⁶, 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, ..., and add NaHCO₃ to pore waters to catalyze olivine carbonation, (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:** Schuiling¹² and Fyfe¹³ 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 hydration⁶. 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 rates⁶. This avoids the cost of maintaining high temperature in a reaction vessel. 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/s⁶.
- **Rapid carbonation may maintain permeability and reactive surface area:** Reactions involving crystallization in pore space could be self-limiting due to armoring of reactive surfaces and decreasing permeability¹⁴⁻²², as observed for hydration and carbonation of basalt^{11, 23-25}. However, outcrops of completely carbonated peridotite (listwanite) show that natural carbonation is not always self-limiting e.g.,^{26, 27}. 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 area⁶, in a process similar cracking caused by salts crystallizing from water in limestone and other building materials^{28, 29} and the similar process of frost cracking³⁰. MacDonald & Fyfe³¹ proposed that increasing solid volume associated with olivine hydration (serpentinization) produces stresses that fracture surrounding rock, as further investigated for serpentinization (e.g.,^{32, 33-36}) and granite weathering³⁷. Reactive cracking may be more likely during rapid mineral carbonation compared to slow carbonation, because increasing stress due to carbonate precipitation in pore space competes with relaxation mechanisms such as viscous deformation of carbonate minerals³⁸. This is consistent with experiments on crystallization of low viscosity³⁹ Na-sulfate salts in porous limestone: Rapid crystallization caused fractures, while slow crystallization did not⁴⁰. 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. Regardless of the merits of the reactive cracking hypothesis, it is known that hydrothermal systems producing serpentine and carbonate from peridotite remain active for tens of thousands of years^{6, 41}. And, even without fracturing, flow-through experiments on carbonation of porous peridotite showed increasing permeability vs time⁴².
- **The added costs for *in situ* peridotite or basalt carbonation (preheating and/or hydrofracturing a rock volume at depth) could be small compared to injection of supercritical CO₂ into pore space** particularly if it is in an area with high heat flow where subsurface peridotite or basalt is already hot, and thermal convection drives fluid circulation. The cost of hydrofracture is probably negligible per ton of CO₂ consumed. The cost of pre-heating a rock volume is significant. 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%. If surface water with atmospheric P_{CO2} is used as a fluid reactant, this avoids the cost of CO₂ capture “at the smokestack” (currently > \$50/ton) and can be used for “negative CO₂ emissions”, similar to “air capture” and unlike CO₂ capture at power plants. However, the

rate enhancement due to temperature and pressure is ~ 100 to 1000 times smaller if sea water rather than CO₂-rich fluid is used as a reactant, so exothermic heating (and reactive cracking?) may be correspondingly reduced.

- **Enormous storage capacity in peridotite:** The Oman ophiolite is ~ 70,000 km³⁴³. ~ 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 more than 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). All of these, except perhaps for the Balkan examples, extend offshore beneath marine sediments. This is particularly evident where peridotite outcrops along the shoreline. In general, near-surface mantle peridotite is present on all continents except perhaps in Antarctica, and for example in North America the cumulative volume of several smaller bodies taken together is comparable to the volume of peridotite in Oman.
- **Basalt carbonation kinetics are uncertain:** Data suggest that carbonation of crystalline basalt is 10 to 100 times slower than peridotite carbonation⁷, which is a problem from the point of view of self-heating and reactive cracking but (a) dissolution of basaltic glass may be much faster than dissolution of crystalline basalt⁴⁴, and (b) peridotite carbonation rates are highest at high NaHCO₃ concentrations^{4,10}, while comparable experiments have not been done on basalt.
- **Enormous storage capacity in basalt:** Mineral carbonation in basalt consumes less CO₂ per kg than in peridotite, but the mass of basalt near the seafloor is enormous. High porosity and permeability in some basaltic lava flows capped by low permeability sediments makes them attractive targets for “conventional” CO₂ storage via injection into pore space^{8,9}. Estimated storage capacities in pore space for deep-sea basalt aquifers overlain by suitable cap rocks include 500-2500 Gt of CO₂ in the Juan de Fuca Ridge region, and 1000-5500 Gt in the Caribbean flood basalt province^{8,9}. Displacement of ambient pore water to the seafloor is far less problematic than displacement of saline fluids from on-land aquifers, and leakage of CO₂ to the seafloor is less problematic than on land. Compared to clastic sediments, basalt has a higher capacity for mineral carbonation, so that large masses of CO₂ injected into basalt will eventually be near-permanently stored in solid carbonate minerals.
- **A lot to do:** It is crucial to gather information on existing alteration, fracture density, stress state, porosity and permeability in near-seafloor peridotite and basalt overlain by a low permeability cap rock, and to explore hydrofracture and CO₂ injection experiments. Offshore targets are plentiful, and there are many synergies between this research and work on igneous accretion of oceanic crust, alteration and deformation of the crust, ocean history, hydrology and biogeochemistry. In the context of IODP planning, we propose an international workshop to choose the best sites for such studies, and to design experiments to test proposed methods for sub-seafloor CO₂ capture and storage. The scope of the workshop should include storage in sedimentary formations, as well as peridotite and basalt. In addition to site identification and experimental design, workshop discussions could include current and future potential for modeling of reactive porous flow, hydrofracture (intentional, to enhance permeability, and unintentional, leading to potentially rapid CO₂ leakage), potential environmental impact, and potential for biogeochemical enhancement of mineral carbonation. IODP effort on this topic is worthwhile and timely because of the potential for permanent, sub-seafloor storage of immense amounts of CO₂.

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