

In situ carbonation of peridotite for CO₂ storage

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The rate of natural carbonation of tectonically exposed mantle peridotite during weathering and low-temperature alteration can be enhanced to develop a significant sink for atmospheric CO₂. Natural carbonation of peridotite in the Samail ophiolite, an uplifted slice of oceanic crust and upper mantle in the Sultanate of Oman, is surprisingly rapid. Carbonate veins in mantle peridotite in Oman have an average ¹⁴C age of ≈26,000 years, and are not 30–95 million years old as previously believed. These data and reconnaissance mapping show that ≈10⁴ to 10⁵ tons per year of atmospheric CO₂ are converted to solid carbonate minerals via peridotite weathering in Oman. Peridotite carbonation can be accelerated via drilling, hydraulic fracture, input of purified CO₂ at elevated pressure, and, in particular, increased temperature at depth. After an initial heating step, CO₂ pumped at 25 or 30 °C can be heated by exothermic carbonation reactions that sustain high temperature and rapid reaction rates at depth with little expenditure of energy. In situ carbonation of peridotite could consume >1 billion tons of CO₂ per year in Oman alone, affording a low-cost, safe, and permanent method to capture and store atmospheric CO₂.

alteration and weathering | carbon capture | exothermic | carbon sequestration | mineral

Recognition that anthropogenic CO₂ input to the atmosphere has substantially increased atmospheric CO₂ concentration, and that increased CO₂ may drive rapid global warming, has focused attention on carbon capture and storage (1). One storage option is conversion of CO₂ gas to stable, solid carbonate minerals such as calcite (CaCO₃) and magnesite (MgCO₃) (2). Natural carbonation of peridotite by weathering and low-temperature alteration is common. Enhanced natural processes in situ may provide an important, hitherto neglected alternative to ex situ mineral carbonation “at the smokestack.” In this article, we evaluate the rate of natural carbonation of mantle peridotite in the Samail ophiolite, Sultanate of Oman, and then show that under certain circumstances exothermic peridotite alteration (serpentinization, carbonation) can sustain high temperature and rapid reaction with carbonation up to 1 million times faster than natural rates, potentially consuming billions of tons of atmospheric CO₂ per year. In situ mineral carbonation for CO₂ storage should be evaluated as an alternative to ex situ methods, because it exploits the chemical potential energy inherent in tectonic exposure of mantle peridotite at the Earth’s surface, does not require extensive transport and treatment of solid reactants, and requires less energy for maintaining optimal temperature and pressure.

Tectonically exposed peridotite from the Earth’s upper mantle, and its hydrous alteration product serpentinite, have been considered promising reactants for conversion of atmospheric CO₂ to solid carbonate (3). However, engineered techniques for ex situ mineral carbonation have many challenges. Kinetics is slow unless olivine and serpentine reactants are ground to powder, heat-treated, and held at elevated pressure and temperature (4).^{*} Pending further improvements, these approaches may be too expensive in financial terms and energy expenditures (5).

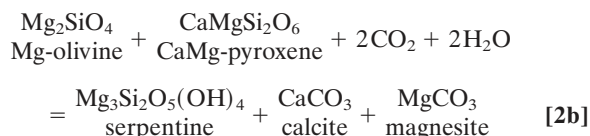
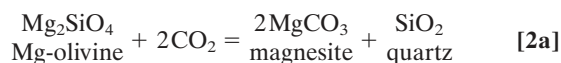
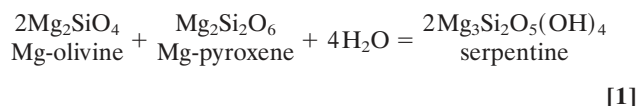
The potential for in situ mineral carbonation in peridotite is emphasized in the following simple calculation. There are ≈2.9·10¹⁵ kg of CO₂ in the atmosphere, up from a preindustrial value of perhaps 2.2·10¹⁵ kg (6). In Oman, the Samail “ophio-

lite”—a thrust-bounded slice of oceanic crust and upper mantle—is >350 km long and ≈40 km wide, and it has an average thickness of ≈5 km (7). Of this volume ≈30% is mantle peridotite. Adding 1 wt% CO₂ to the peridotite would consume ¼ of all atmospheric CO₂, an amount approximately equivalent to the increase since the industrial revolution. Converting all Mg cations in the peridotite to carbonate would consume ≈7·10¹⁶ kg (77 trillion tons) of CO₂. Similarly large ophiolites are in Papua New Guinea (≈200 × 50 km in area), New Caledonia (≈150 × 40 km), and along the east coast of the Adriatic Sea (several ≈100 × 40 km massifs).

Mantle peridotite is ordinarily beneath the Earth’s crust, >6 km below the seafloor and 40 km below the land surface. It is strongly out of equilibrium with air and water at the Earth’s surface. Its exposure via large thrust faults along tectonic plate boundaries creates a reservoir of chemical potential energy. Fyfe (8) proposed that exothermic hydration (forming serpentine minerals) can heat peridotite. His idea has recently been invoked to explain the heat source for ≈90 °C fluids at the Lost City hydrothermal vent system near the Mid-Atlantic Ridge (9), and evaluated theoretically (10, 11). Below, we show that carbonation of peridotite generates more power than hydration because of larger enthalpy changes and faster reactions between 25 and 200 °C. Temperatures necessary for rapid reaction can be sustained via exothermic carbonation, instead of an external heat source.

Natural Peridotite Hydration and Carbonation

Mantle peridotite is composed largely of the minerals olivine [(Mg,Fe)₂SiO₄] and pyroxene [(Ca,Mg,Fe)₂Si₂O₆], which react with H₂O and CO₂ near the Earth’s surface to form hydrous silicates (serpentine), Fe-oxides (magnetite), and carbonates (calcite, magnesite, and dolomite). Such reactions may generally be formulated as:



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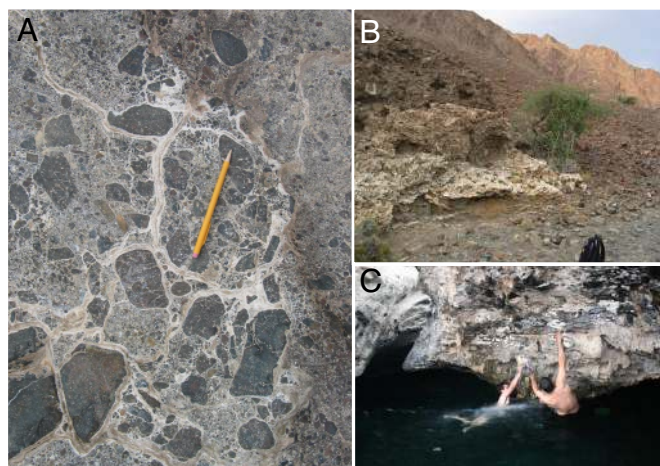


Fig. 4. Carbonate veins and massive travertine “inflating” carbonate-cemented, peridotite cobble conglomerate (A; 22.9845°N, 58.6322°E) and young alluvial fan deposits (B; 22.902°N, 58.371°E). Sampling stalactites forming beneath overhang in peridotite cobble conglomerate (C; 22.9875°N, 22.6327°E).

minerals in 2 ways. First, we can estimate the mass of veins directly, and divide this by their average age. Poupeau *et al.* (29) estimated an erosional denudation rate of ≈ 0.3 mm/yr for northern Oman. The ages of carbonate veins in peridotite suggest that veins form mainly in a thin weathering horizon that keeps pace with erosion; this horizon must generally be ≈ 15 m thick (erosion rate ≈ 0.0003 m/yr \cdot maximum age of carbonate veins $\approx 50,000$ years). Newly created road cuts in Oman peridotites reveal abundant, submillimeter carbonate veins on joint surfaces. We measured the vein abundance as ≈ 1 vol% in transects along road cuts (Table S2); 1% of the volume of a 15-m-thick weathering horizon in the Oman peridotite corresponds to $\approx 10^{12}$ kg of CO_2 , for an average CO_2 uptake of $\approx 4 \cdot 10^7$ kg/yr.

We can independently estimate the mass of travertine formed at and near the surface by alkaline springs, and infer the associated mass of carbonate veins far from the surface that must be formed during recharge of these springs. Based on our relatively detailed, although incomplete, mapping in the southern third of the ophiolite, we estimate that there are ≈ 45 travertine terraces in the Samail ophiolite (Fig. 2) that are ≈ 1 m thick, with exposed areas $\approx 200,000$ m² (Fig. S1), comprising a total of $\approx 10^7$ m³ of exposed travertine. Travertine extends beneath alluvium downslope from outcrop areas, and travertine deposits are underlain by a zone ≈ 10 m thick with $\approx 5\%$ calcite-rich veins (Table S2), so that their total volume is probably ≈ 2.5 times the exposed volume. Near-surface deposits, similar in composition and age to the travertine terraces, occur as massive carbonate bands, veins, and cement in alluvial terraces and conglomerates with peridotite clasts (Fig. 4). The volume of carbonate cement derived from Ca-OH^- waters in peridotite sediments is hard to estimate, but is at least as large as the volume of travertine terraces. All of these factors, taken together, suggest that the volume of near-surface travertine and carbonate in peridotite sediments in Oman is $\approx 5.5 \cdot 10^7$ m³ or more, corresponding to at least $\approx 10^{11}$ kg of CO_2 .

Spring waters and shallow groundwater in peridotite catchments fall into 2 compositional groups, as discussed above and illustrated in Fig. S2. We can estimate carbonation rates from water compositions, assuming (i) all carbon in type 1 waters is consumed to form solid carbonate during formation of type 2 waters, and (ii) the difference in Ca between type 2 and type 1 waters is precipitated as calcite when type 2 waters reach the

surface. In California, type 1 waters have ≈ 0.2 mmol of Ca per liter, and up to 24 mmol of carbon per liter (19). Type 2 waters have essentially no carbon, and ≈ 1.5 mmol Ca per liter (Fig. S2). Thus, for every mole of calcite near the surface, up to $\approx 24/(1.5-0.2)$ or 18 mol of magnesite form in the subsurface.

There is a maximum of ≈ 8 mmol/L, carbon in Oman Type 1 waters, lower than in California, whereas Ca concentration is ≈ 0.8 mmol/L, higher than in California. There is essentially no carbon, and ≈ 1.6 mmol Ca in type 2 waters in Oman. It is not clear whether these values reflect lower carbon concentrations in Oman waters compared with those in California, or whether end-member type 1 waters in Oman have not yet been sampled. If, for every mole of near-surface calcite, 8/(1.6–0.8) or 10 mol of magnesite are precipitated as veins, this yields $\approx 10^{12}$ kg of CO_2 in veins, consistent with the estimate derived from measured vein abundance and the inferred thickness of the veined horizon.

In summary, estimates of the volume of carbonate deposits formed during ongoing weathering of peridotite, and their average age of 26,000 years, indicate that $\approx 4 \cdot 10^7$ kg of atmospheric CO_2 per year are consumed via mineral carbonation in the Samail ophiolite, or ≈ 2 tons/km³ of peridotite. This strikingly rapid rate is compared with CO_2 flux in rainwater and groundwater, and discussed further in the *SI Text*. Here, we emphasize that a factor of 100,000 increase in this rate could consume 4 billion tons of CO_2 per year, $\approx 10\%$ of the annual increase in atmospheric CO_2 because of anthropogenic emissions, via carbonation of peridotite in Oman.

Enhancing Rates of Peridotite Carbonation in Situ

In this section, we propose and evaluate ways to increase CO_2 uptake in situ in tectonically exposed peridotite massifs. In the Samail ophiolite and other large massifs, an obvious approach is to increase the depth of the weathering horizon by a factor of 200, from ≈ 15 m to ≈ 3 km in the peridotite via drilling and hydraulic fracture (30). Additional fracture may be anticipated as a result of thermal expansion during heating (31), volume increase during hydration (32–34), and volume increase during carbonation. Carbonation of olivine (Eq. 2b) results in $\approx 44\%$ increase in the solid volume, which can lead to enormous stresses that may be relieved by cracking and additional expansion (Fig. 1 B and C).

An additional increase in the carbonation rate, by a factor of $> \approx 10^6$, could be achieved by raising the temperature of the peridotite and injecting CO_2 -rich fluids. There is an optimal temperature for peridotite carbonation. Heating from low temperature speeds the diffusive kinetics of hydration and carbonation. However, the chemical potential driving the reaction is reduced as the temperature approaches the equilibrium phase boundary for serpentine or carbonate mineral stability. The combined effect yields a maximum reaction rate at a temperature intermediate between surface conditions and the equilibrium phase boundary (Fig. S3). The reaction rate for serpentinization as a function of temperature has a maximum value at $\approx 260^\circ\text{C}$ over a range of pressure (35), whereas the rate of carbonation is optimized at, for example, 185°C and 150 bars CO_2 pressure.* We fit data on rates of serpentinization of olivine with grain size 58–79 μm (35) and carbonation of olivine with grain size $\leq 75 \mu\text{m}$ * as a function of temperature and CO_2 partial pressure, yielding a serpentinization rate (Fig. S4)

$$\Gamma = 0.00000100 \exp[-0.000209(T - 260^\circ\text{C})^2] \quad [3]$$

and a carbonation rate (Fig. S5 and Fig. S6).

$$\Gamma \sim 1.15 \cdot 10^{-5} (P(\text{CO}_2), \text{bars})^{1/2} \exp[-0.000334(T - 185^\circ\text{C})^2] \quad [4]$$

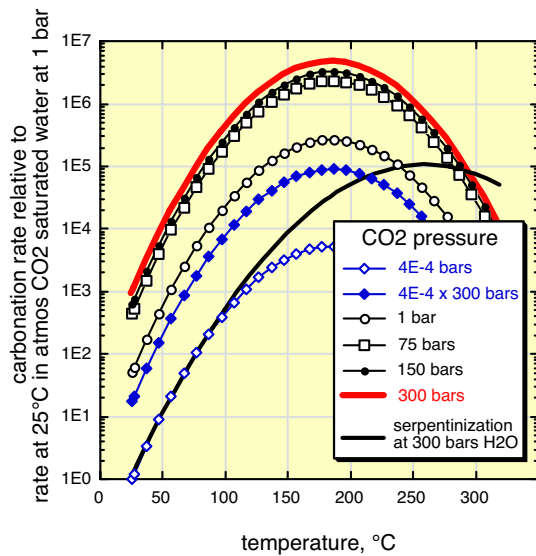


Fig. 5. Rates of olivine carbonation (lines and symbols) and serpentinization (black line, no symbols) as a function of temperature and pressure, compared with the rates at 25 °C for surface water equilibrated with the atmosphere at 1 bar. A range of curves are shown for carbonation, with a single curve for serpentinization of olivine saturated in aqueous fluid at 300 bars. Note that the reaction rate for carbonation is much higher than that for serpentinization at 300 bars and temperature < ≈ 250 °C. The enthalpy change, per kilogram, is also ≈ 3 times larger for carbonation than for serpentinization (see text).

both in units of mass fraction per second. Heating and raising the partial pressure of CO₂ can increase the carbonation rate by a factor of $>10^6$ (Fig. 5), and with the potential for increasing the

thickness of the weathering horizon by fracturing, the overall increase could be a factor of $\approx 10^9$. Together with the estimated present-day CO₂ uptake at the end of the previous section, this corresponds to $2 \cdot 10^9$ tons/km³ per year.

Thermal Effects of Advection, Diffusion, and Reaction

The change in temperature for a particular volume in a subsurface, porous aquifer can be approximated in 1 dimension as

$$dT/dt = (T_{in} - T) \rho_f C_p^f \phi w / (\rho_s C_p^s d) - (T - T_o) \kappa / d^2 + \Gamma(T) A \Delta H / [C_p^s (1 - \phi) + C_p^f (\phi)] \quad [5]$$

where T_{in} is the temperature of incoming water or aqueous fluid (°C or Kelvin), T is the current temperature in the volume, T_o is the far-field temperature, outside the volume, which is equal to the initial temperature in the volume, ρ_f and ρ_s are the densities of the fluid and solid, C_p^f and C_p^s are the heat capacities of the fluid and solid, ϕ is the porosity or volume fraction of fluid (nondimensional, 1% in all calculations shown here), w is the fluid flow velocity (m/s), d is the dimension or “size” of the volume (m , 1,000 m in all calculations shown here), κ is the thermal diffusivity (10^{-6} m²/s), Γ is the reaction rate, which is a function of temperature (units of 1/s), A is the fraction of the rock available for reaction in the volume (nondimensional), and ΔH is the enthalpy change due to reaction. The use of a reactive volume fraction term < 1 accounts for the fact that most natural rocks do not have an effective grain size of ≈ 70 μ m, unlike the experiments used to calibrate Eqs. 3 and 4. The volume available for reaction is product of a diffusion distance times the surface area of grains. The surface area is proportional to the radius squared, so the use of a reactive volume fraction of 0.01% corresponds to modeling of an effective “grain size” or fracture spacing of ≈ 7 mm, 100 times larger than in the experiments.

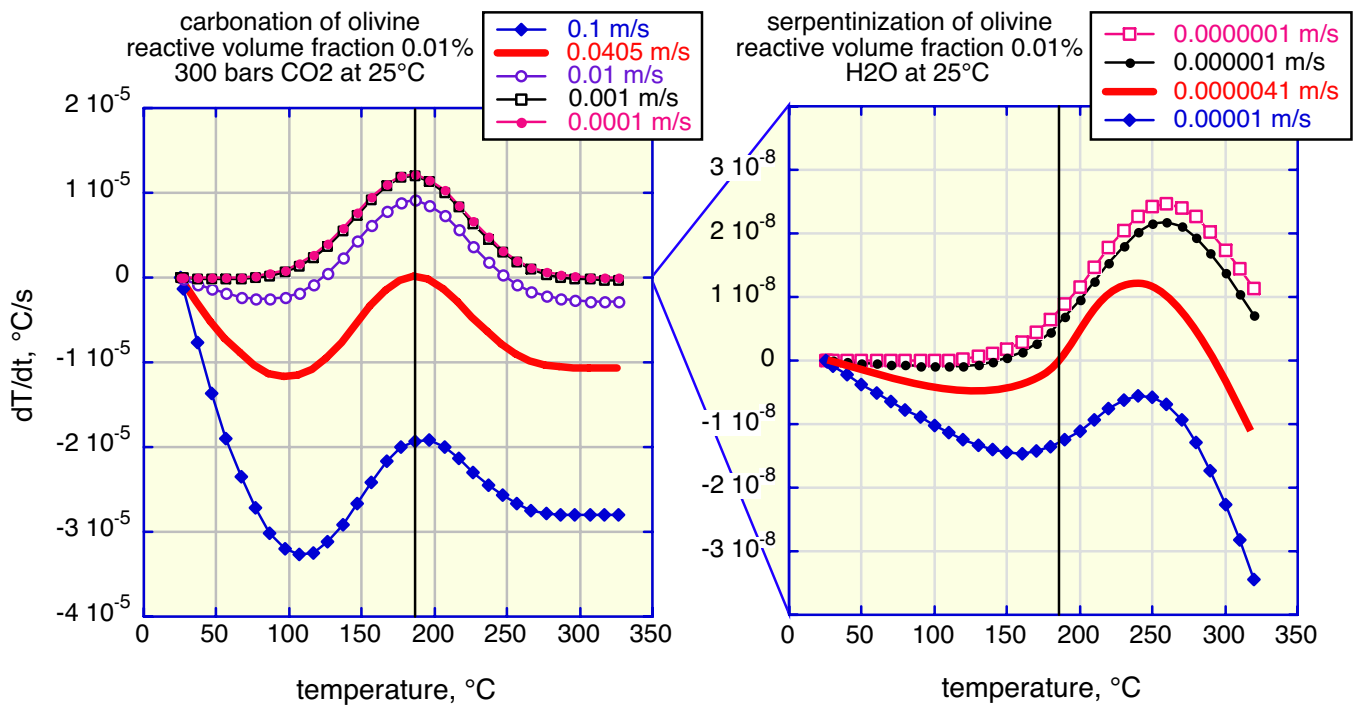


Fig. 6. Calculated rate of change of temperature due to olivine carbonation (Left) and serpentinization (Right) at 300 bars as a function of rock temperature and fluid flow rate, for 25 °C fluid and a reactive volume fraction of 0.01%, from our 1-dimensional energy balance model (Eq. 5). A constant rock temperature of 185 °C can be maintained by pumping 25 °C CO₂ at ≈ 0.040 m/s, or by pumping 25 °C H₂O at $\approx 4.1 \cdot 10^{-6}$ m/s. Note that the range of temperature derivatives and steady-state flow rates at 185 °C are much larger for the olivine carbonation reaction than for serpentinization.

of sediment offshore. Here, peridotite could be drilled and fractured, and a volume could be heated. Again, little heating would be required if, for example, the initial temperature at the bottom of a 5-km bore hole is 100 °C (Fig. 8). Then, controlled convection of near-surface water through the rock volume could sustain high temperature via exothermic hydration of olivine at a flow rate of $\approx 4 \cdot 10^{-6}$ m/s (as seen in Fig. 3 *Right*). The carbonation rate would be limited by supply of dissolved CO₂ in convecting seawater—only $\approx 10^4$ tons of CO₂ per km³ of peridotite per year at a flow rate of $4 \cdot 10^{-6}$ m/s—but the cost would be relatively low.

Conclusion: Promising Alternatives to ex Situ Mineral Carbonation

Because these proposed methods of in situ mineral carbonation use the chemical potential energy inherent in tectonic exposure of mantle peridotite at the Earth's surface, the optimal temperature for carbonation can be maintained in a rock volume at little expense. Further, rock volumes at depth are, inherently, at relatively high pressure and elevated temperature. Thus, compared with engineered, mineral carbonation “at the smoke-stack,” this method does not involve quarrying and transportation of peridotite, processing of solid reactants via grinding and heat treatment, or maintaining high temperature and pressure in a reaction vessel. Instead, the major energy investments in this method would be for drilling, hydraulic fracturing, pumping fluid, preheating fluid for the first heating step, and purification

of CO₂. Also, unlike ex situ mineral carbonation, this method may require on-site CO₂ capture or transport of purified CO₂ to the in situ carbonation locality.

Clearly, more elaborate models combined with field tests will be required to evaluate and optimize this method. For example, it is difficult to predict the consequences of hydraulic fracturing of peridotite, plus cracking associated with heating, hydration, and carbonation, in terms of permeability and reactive volume fraction. Such processes are all-but-impossible to simulate in the laboratory. Large-scale field tests should be conducted, because the proposed method of enhanced natural CO₂ sequestration provides a promising potential alternative to storage of supercritical CO₂ fluid in underground pore space, and to engineered, ex situ mineral carbonation.

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