

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).

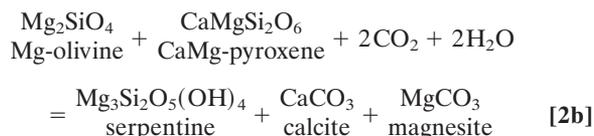
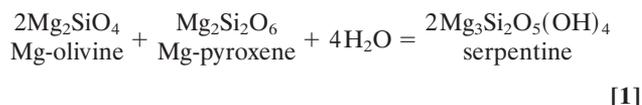
The potential for in situ mineral carbonation in peridotite is emphasized in the following simple calculation. There are ≈2.9·10¹⁵ kg of CO₂ in the atmosphere, up from a preindustrial value of perhaps 2.2·10¹⁵ kg (6). In Oman, the Samail “ophio-

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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Conflict of interest statement: P.B.K. and J.M. have a preliminary patent filing for the technique of heating peridotite to achieve self-sustaining, rapid carbonation.

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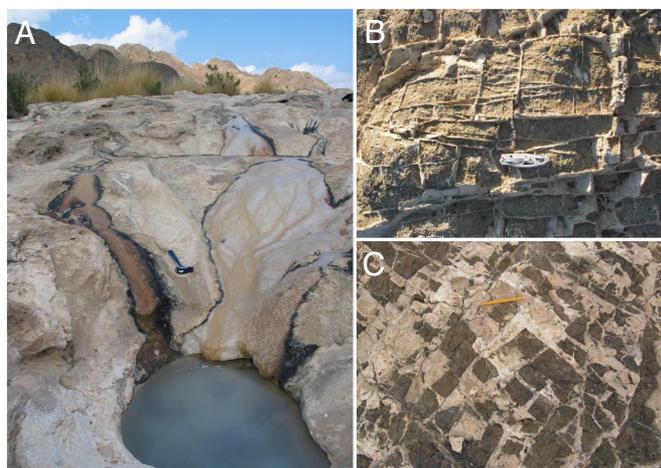


Fig. 1. Photographs of travertine and carbonate veins in Oman. (A) Actively depositing travertine near the village of Falaj (22.846°N, 58.056°E) with rock hammer for scale, altered peridotite in the background. (B) White carbonate veins weathering out in positive relief in altered peridotite at “Duck” (22.815°N, 58.838°E) with pocket knife for scale. (C) White carbonate veins in altered peridotite north of the village of Batin (22.925°N, 58.671°E) with pencil for scale.

Evidence for natural, low-temperature hydration and carbonation of mantle peridotite can be found in springs and associated travertines in catchments composed of mantle peridotite (12–19), and in outcrops of altered peridotite with abundant carbonate veins (e.g., refs. 20–26). High alkalinity, stable isotope ratios, and formation of travertine and carbonate cemented conglomerates in springs (Fig. 1A) indicate ongoing serpentinization involving meteoric water at low temperature. In addition to travertine at springs, carbonate veins are also found within host peridotite (Fig. 1B and C).

Vein and travertine formation are linked (e.g., refs. 15–19). Groundwater reacting with peridotite in near-surface, open systems forms water rich in Mg and HCO_3^- , which we call *Type 1* waters, according to Barnes and O’Neil (18). When these waters become isolated from the atmosphere, continued reaction with peridotite leads to precipitation of abundant magnesite and dolomite as veins; the resulting waters become progressively richer in Ca and OH^- , and impoverished in dissolved carbon, approaching a pH of 12. When these Ca- OH^- -rich, carbon-poor, *Type 2* waters emerge near the surface, to mix with Mg- HCO_3^- waters or react with the atmosphere, they precipitate abundant calcite and dolomite in near-surface veins, carbonate cement in unconsolidated sediment, and travertine.

Rate of Peridotite Carbonation in the Samail Ophiolite, Oman

The rate of CO_2 uptake via weathering of peridotite is poorly known. We sampled solid carbonate forming from peridotite over a wide area in the Samail ophiolite [Fig. 2 and supporting information (SI) Table S1], including veins from ridges far from present day springs as well as currently forming travertine. Previous workers inferred that most veins far from present-day springs are 30–90 million years old, related to formation of oceanic crust, emplacement of the ophiolite, and Eocene extension (e.g., refs. 15, 21, 22, 27). However, all of our samples have ^{14}C ages from 1,600 to 43,000 years, similar to the previously measured range of 840 to 36,000 years in the vicinity of a single, actively forming travertine in Oman (28). Samples of veins from ridges are mainly composed of dolomite and magnesite. In general, they are somewhat older than calcite-rich travertine and calcite-dolomite veins near active springs. However, the vein

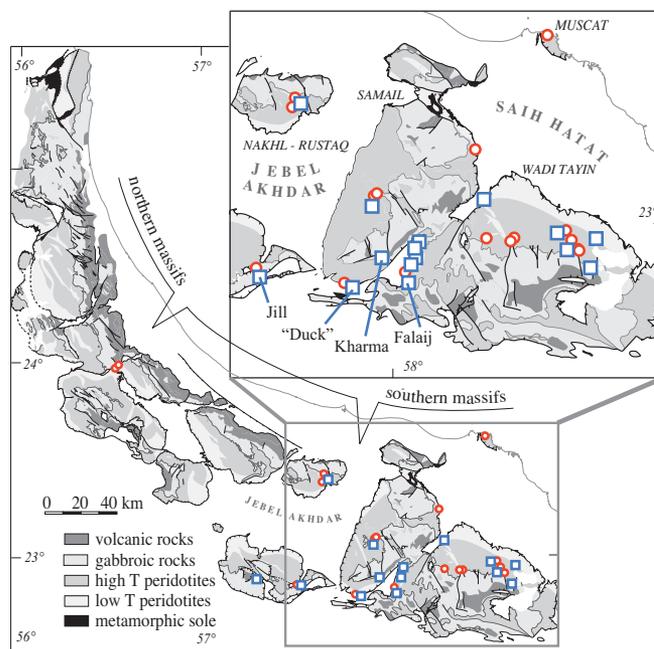


Fig. 2. Geologic map of the Oman ophiolite (8), with locations of carbonate samples dated by using ^{14}C (red circles, Table S1) and locations of known travertine deposits in the Bahla, Samail, and Wadi Tayin ophiolite massifs [blue squares; for perimeter maps of the “Duck,” Kharma and Falaj travertines, see Fig. S1; for more information on the Jill travertine deposit, see Clark and Fontes (28)]. Based on our observations of these 3 southernmost massifs, we infer that there are at least 45 similar travertine deposits in the entire ophiolite. We only show locations of travertine deposits that we have personally observed, and there are probably many more even in the southern massifs. In addition to travertine deposits on the surface (Fig. 1A, with locations shown here), there are thick travertine deposits forming within alluvial and gravel terraces (examples in Fig. 4).

samples have an average age of $\approx 26,000$ years, with a fairly “flat” age distribution (Fig. 3), and none are too old to date with ^{14}C .

The observed volume of carbonate terraces and veins in the Samail ophiolite, together with their ages, can be used to estimate the rate of CO_2 uptake via formation of solid carbonate

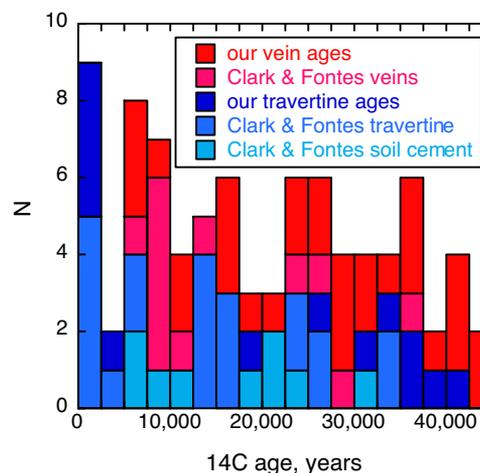


Fig. 3. Combined histogram of ^{14}C ages for our samples (Fig. 2, Table S1) and those of Clark and Fontes (28). The Clark and Fontes samples were taken from a single actively forming travertine deposit near the village of Jill, and carbonate veins in the underlying peridotite within a few meters of the travertine.

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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