

November 3, 2008

To whom it may concern,

The following is a paper in the Proceedings of the [US] National Academy of Sciences. The methods described in this paper are proprietary. These methods are the property of Columbia University, with US patents pending. We will gladly share details of this method, and the ongoing modeling effort associated with it, in order to pursue the mutual benefit of testing this method. If the method is to be developed for commercial use, then separate arrangements must be made.

Sincerely,

A handwritten signature in black ink, appearing to read "Peter B. Kelemen". The signature is written in a cursive style with a large initial "P" and a long horizontal stroke at the end.

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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).

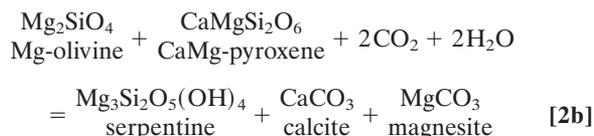
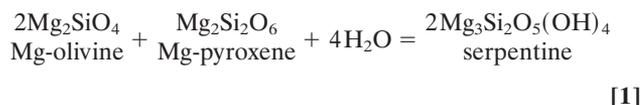
The potential for in situ mineral carbonation in peridotite is emphasized in the following simple calculation. There are ≈2.9·10¹⁵ kg of CO₂ in the atmosphere, up from a preindustrial value of perhaps 2.2·10¹⁵ kg (6). In Oman, the Samail “ophio-

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:



Author contributions: P.B.K. and J.M. designed research, performed research, analyzed data, and wrote the paper.

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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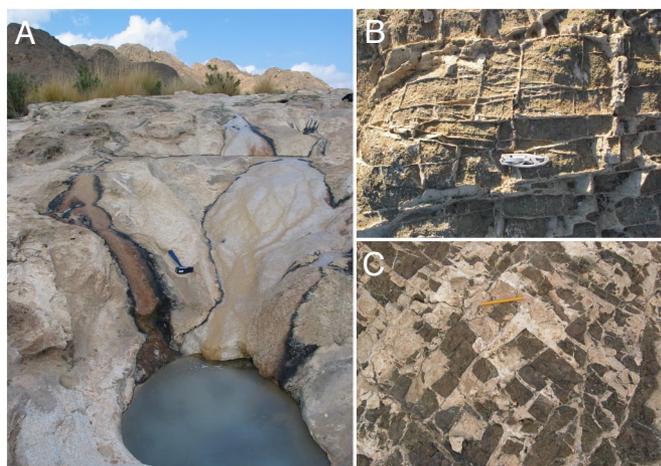


Fig. 1. Photographs of travertine and carbonate veins in Oman. (A) Actively depositing travertine near the village of Falaj (22.846°N, 58.056°E) with rock hammer for scale, altered peridotite in the background. (B) White carbonate veins weathering out in positive relief in altered peridotite at “Duck”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

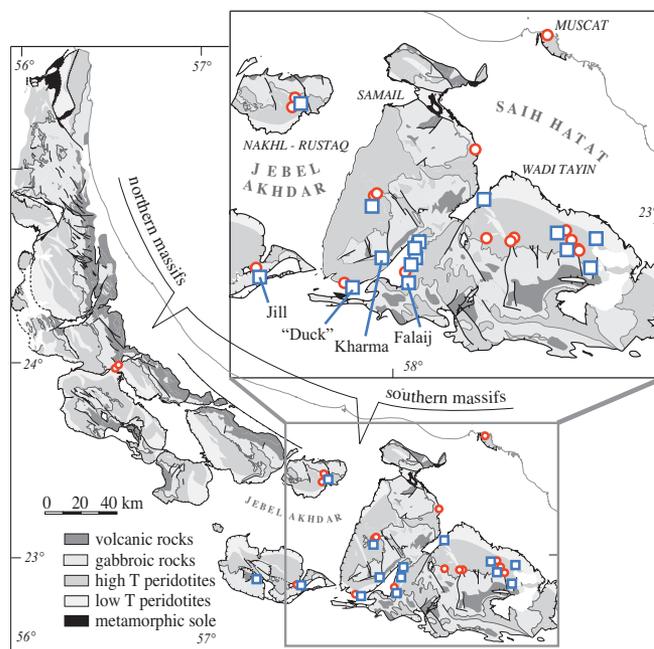


Fig. 2. Geologic map of the Oman ophiolite (8), with locations of carbonate samples dated by using ^{14}C (red circles, Table S1) and locations of known travertine deposits in the Bahla, Samail, and Wadi Tayin ophiolite massifs [blue squares; for perimeter maps of the “Duck,” Kharma and Falaj travertines, see Fig. S1; for more information on the Jil 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

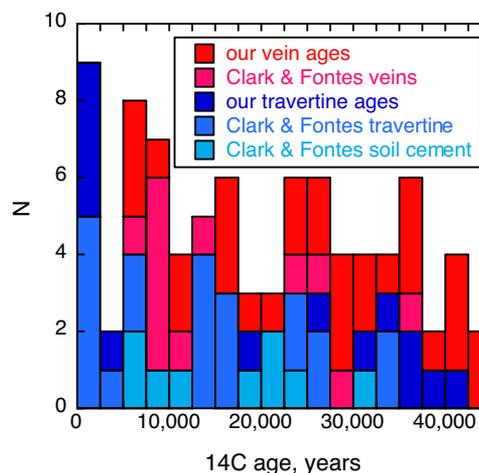


Fig. 3. Combined histogram of ^{14}C ages for our samples (Fig. 2, Table S1) and those of Clark and Fontes (28). The Clark and Fontes samples were taken from a single actively forming travertine deposit near the village of Jil, and carbonate veins in the underlying peridotite within a few meters of the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

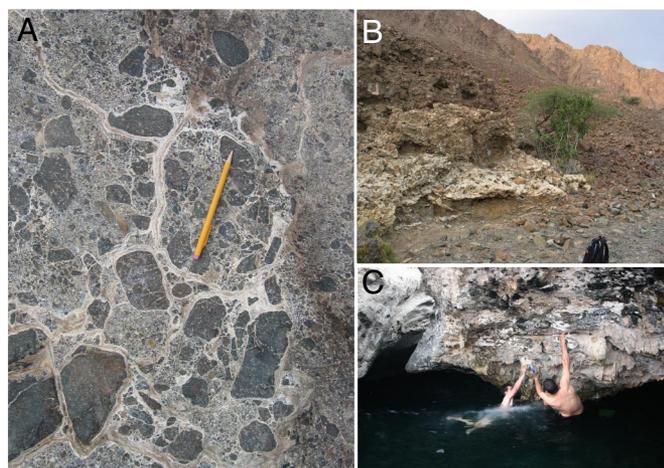


Fig. 4. Carbonate veins and massive travertine “inflating” carbonate-cemented, peridotite cobble conglomerate (A; 22.9845°N, 58.6322°E) and young alluvial fan deposits (B; 22.902°N, 58.371°E). Sampling stalactites forming beneath overhang in peridotite cobble conglomerate (C; 22.9875°N, 22.6327°E).

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).

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

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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Supporting Information

Kelemen and Matter 10.1073/pnas.0805794105

SI Text

Discussion of Rate of Magnesite and Dolomite Formation via Mineral Carbonation in Oman Peridotite. The rapid rate of formation of carbonate minerals via weathering of peridotite in Oman, consuming $\approx 4 \cdot 10^7$ kg of CO_2 per year, is striking for 2 reasons. First, it is faster than the influx of CO_2 dissolved in rainwater. Second, the veins are composed mainly of magnesite and dolomite, which are rare in Phanerozoic sedimentation.

Rainfall over the ophiolite ranges from 50 to 300 mm/yr (1, 2). The interannual variability is large, but this range is likely to have been roughly constant for most of the past 75,000 years with the exception of the “early Holocene humid period” from ≈ 9 to 8 ka (e.g., refs. 3 and 4). CO_2 concentration (all C as CO_2 , for simplicity) is ≈ 1 ppm in rainwater over the ophiolite (5), yielding an annual flux of $\approx 1 \cdot 10^6$ kg of CO_2 from rainfall onto peridotite. Thus, even if all CO_2 in rainwater were consumed to form carbonate via peridotite weathering, this would be 40 times less than observed, estimated consumption of CO_2 via weathering.

In contrast, typical groundwater in the Oman ophiolite contains ≈ 200 ppm CO_2 (5). These are called type 1 waters in the main text, according to Barnes and O’Neil (6). Conversion of rainwater to groundwater takes place via near-surface weathering in an open system. As Mg and Ca concentrations in groundwater rise via water/rock reaction, this causes increased CO_2 uptake into the waters from the atmosphere (e.g., ref. 7). If all rainwater falling on the peridotite is modified to form typical groundwater, then precipitation of $\approx 20\%$ of the CO_2 from groundwater—to form carbonate during continued, closed-

system evolution of the groundwater to form type 2 alkaline spring water (7)—is required to explain the observed, estimated consumption of CO_2 via weathering.

Formation of strata-bound magnesite (MgCO_3) and dolomite ($\text{Ca}_{0.5}\text{Mg}_{0.5}\text{CO}_3$) in sedimentary sections was common early in Earth history, and is rare today, for reasons that continue to be the subject of active research, and this is known as the “Dolomite Problem” (8–11). There is a similar “Magnesite Problem” (12). Ca-Mg carbonate precipitation has recently been observed in highly reduced waters, where it is biologically catalyzed (13–20), including waters in weathering peridotite (21). It is possible that the unexpectedly rapid formation of magnesite and dolomite veins in peridotite of the Oman ophiolite is facilitated by microorganisms, and this should be an area of intensive future research, because these biological processes could perhaps be enhanced to facilitate CO_2 capture and storage.

However, it is not clear that the Dolomite Problem in understanding the kinetics of dolomite and magnesite formation within sedimentary sections extends to the formation of Mg-carbonate veins in peridotite, which may have been rapid and common throughout Earth history. We are not aware of any data on this topic. The kinetic experiments on olivine carbonation (Gerdemann SJ, Dahlin DC, O’Connor WK, Penner LR, Second Annual Conference on Carbon Sequestration, Alexandria, VA, May 5–8, 2003. Report no. DOE/ARC-2003-018, OSTI ID: 898299 8 pp) that underlie our model for enhanced in situ carbonation did not involve biologically catalyzed carbonation, and they yield rates that are approximately consistent with observed rates in Oman.

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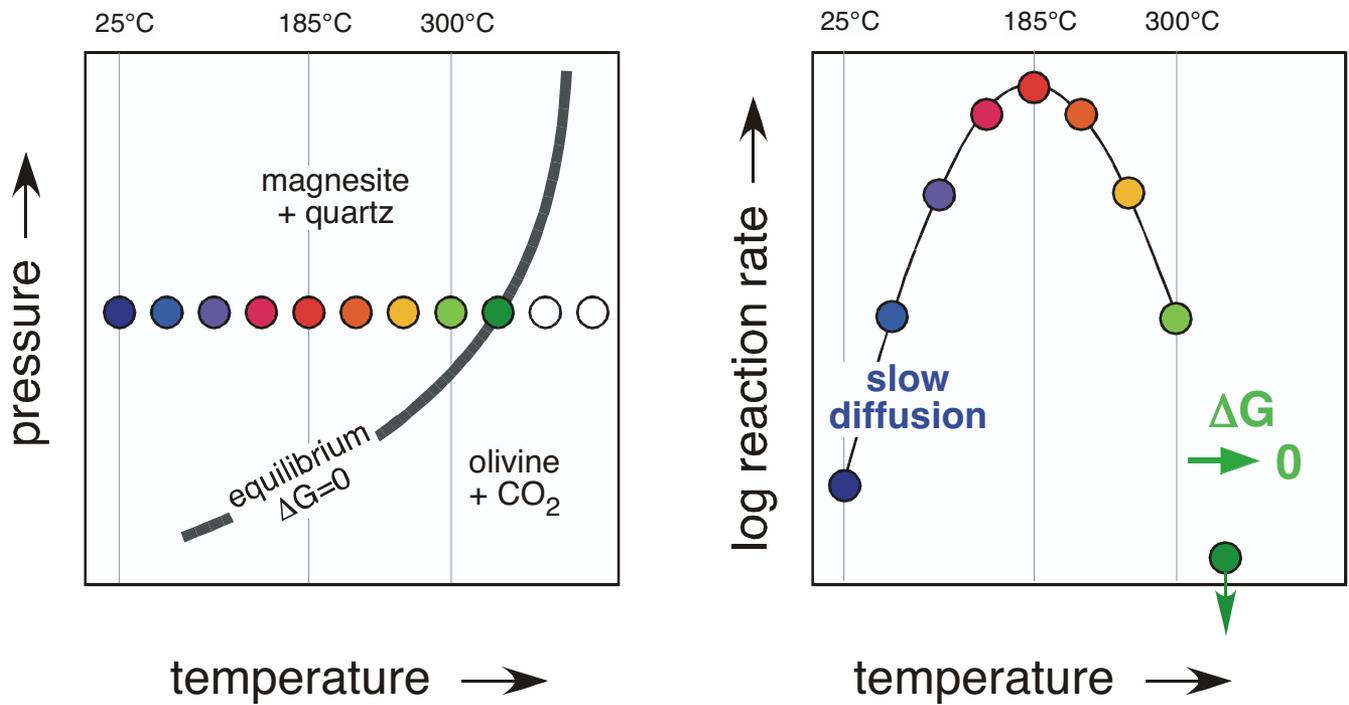


Fig. S3. Schematic illustration of the carbonation rate of olivine (Eq. 2a). At low temperature, the reaction rate is limited by slow diffusion of chemical components. At higher temperature, the chemical potential driving reaction approaches zero at the equilibrium phase boundary. Thus, the maximum reaction rate is at a temperature intermediate between surface conditions and the equilibrium phase boundary. For experimental data illustrating this point, see Gerdemann *et al.* (Second Annual Conference on Carbon Sequestration, Alexandria, VA, May 5–8, 2003. Report no. DOE/ARC-2003-018, OSTI ID: 898299 8 pp).

Martin & Fyfe, 1970 data
 our fit to data, 700 to 3000 bars H₂O

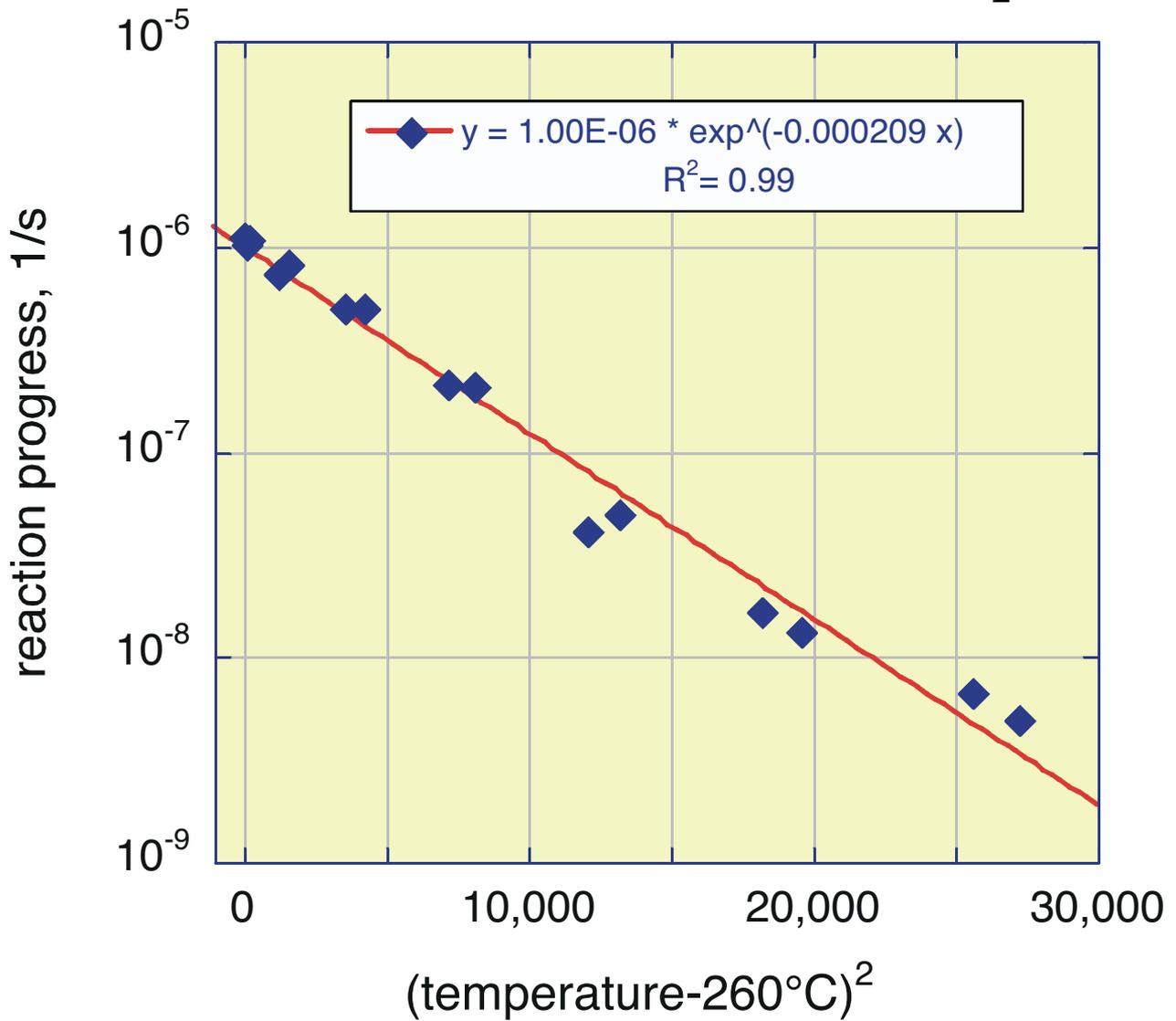


Fig. 54. Our fit to the data of Martin and Fyfe (29) on serpentinization of 58–79 μm olivine powder at 700–3,000 bars of H₂O pressure.

Gerdemann et al., 2003 data
our fit to data, 150 bars CO₂

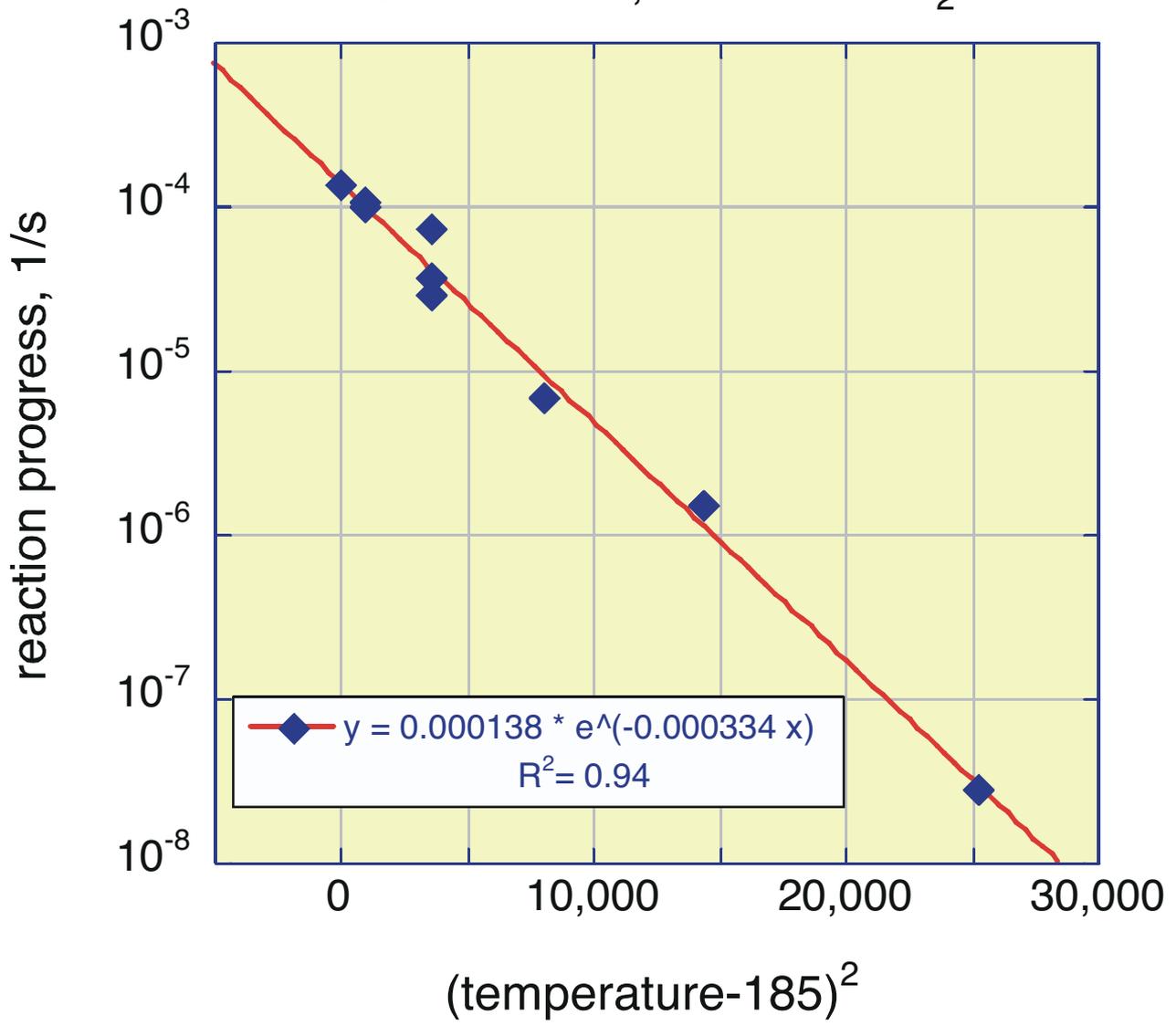


Fig. S5. Our fit to the data of Gerdemann et al. (Second Annual Conference on Carbon Sequestration, Alexandria, VA, May 5–8, 2003. Report no. DOE/ARC-2003-018, OSTI ID: 898299 8 pp) on carbonation of <75 μm olivine powder at 150 bars CO₂.

Table S1. Summary of new ^{14}C geochronology data with sample locations and compositions

| Our sample no. | NOSAMS accession no. | Sample type | Location | Description | Latitude, °N | Longitude, °E | Elevation, m | Fraction modern, C | Frac mod uncertainty | ^{14}C age, yrs | Age uncertainty, yrs | $\delta^{13}\text{C}$ ‰, VPDB | Travertine or vein | Minerals most to least abundant, <10% in italics |
|----------------|----------------------|-------------|----------------------------|---|--------------|---------------|--------------|--------------------|----------------------|--------------------------|----------------------|-------------------------------|--------------------|--|
| OM07-01 | OS-60068 | fragments | mtns betw Muttrah & Muscat | carbonate vein on fault in Muscat | 23.616 | 58.574 | ≈ 115 | 0.0494 | 0.0006 | 24,200 | 100 | -5.56 | vein | |
| OM07-02 | OS-60117 | fragments | mtns betw Muttrah & Muscat | carbonate vein on fault in Muscat | 23.616 | 58.574 | ≈ 115 | 0.0251 | 0.0008 | 29,600 | 250 | -10.14 | vein | |
| OM07-03 | OS-60071 | fragments | Wadi Bani Karous/Al Abyad | carbonate vein on fault | 23.39018 | 57.65915 | 307 | 0.0063 | 0.0004 | 40,700 | 460 | -7.47 | vein | |
| OM07-04 | OS-60074 | fragments | Wadi Bani Karous/Al Abyad | some alteration associated with carbonate veins | 23.43000 | 57.66816 | 269 | 0.0113 | 0.0004 | 36,000 | 280 | 2.5 | vein | |
| OM07-05 | OS-59332 | powder | Sohar to Wuqbah highway | carbonate veins in serpentine | 23.98770 | 56.52079 | 417 | 0.0171 | 0.0004 | 32,700 | 190 | -6.17 | vein | dol,serp, cct,grn |
| OM07-07 | OS-59337 | powder | Sohar to Wuqbah highway | carb vein in serpentine, massive compared to 05, ≤ 10 cm thick | 23.97561 | 56.50196 | 472 | 0.0050 | 0.0002 | 42,600 | 360 | -9.72 | vein | mag,dol |
| dup OM07-07 | OS-60072 | fragments | Sohar to Wuqbah highway | carb vein in serpentine | 23.97561 | 56.50196 | 472 | 0.0203 | 0.0004 | 31,300 | 160 | -9.55 | vein | mag,dol |
| OM07-08 | OS-60013 | powder | village of Jill | erosional remnant above level of travertine terrace | 22.86339 | 57.51501 | 483 | 0.0066 | 0.0003 | 40,400 | 310 | -15.93 | trav | cct,serp |
| dup OM07-08 | OS-60191 | fragments | village of Jill | erosional remnant above level of travertine terrace | 22.86339 | 57.51501 | 483 | 0.0094 | 0.0003 | 37,500 | 260 | -15.74 | trav | cct,serp |
| OM07-09 | OS-60110 | powder | village of Jill | 2 m below 08 on currently active travertine | 22.86339 | 57.51501 | 482 | 0.0369 | 0.0005 | 26,500 | 120 | -16.51 | trav | |
| OM07-10 | OS-60021 | fragments | village of Jill | small globular carbonate on top of the travertine sequence | 22.86339 | 57.51501 | 482 | 0.7460 | 0.0040 | 2,350 | 40 | -27.21 | trav | |
| OM07-11B | OS-60076 | fragments | village of Jill | three different stalactites one meter below 09 | 22.86300 | 57.51475 | 481 | 0.7535 | 0.0027 | 2,270 | 30 | -22.8 | trav | |
| OM07-12 | OS-60069 | powder | village of Jill | carbonate veins in serpentine, 1 m below stalagmites | 22.86300 | 57.51476 | 481 | 0.0277 | 0.0005 | 28,800 | 150 | -12.3 | vein nr trav | cct,serp |
| OM07-13 | OS-60070 | powder | village of Jill | between 11 and 12 | 22.86302 | 57.51478 | 482 | 0.0163 | 0.0003 | 33,100 | 140 | -9.91 | trav | cct,serp,grn |
| OM07-14 | OS-60015 | powder | village of Jill | very base of outcrop area, in wadi | 22.86274 | 57.51494 | 478 | 0.6328 | 0.0023 | 3,670 | 30 | -3.36 | trav | cct,serp,dol,qtz,kao,grn |
| OM07-16 | OS-59338 | powder | "Duck" outcrop | top of eroded outlier in travertine terrace | 22.81464 | 57.83808 | ≈ 480 | 0.0105 | 0.0003 | 36,600 | 240 | -12.44 | trav | cct,serp,dol,grn,kao |
| OM07-17 | OS-60118 | powder | "Duck" outcrop | carbonate vein in serpentine | 22.81464 | 57.83808 | ≈ 480 | 0.4901 | 0.0020 | 5,730 | 35 | -0.12 | vein nr trav | dol,cct,serp,grn,kao |
| OM07-18 | OS-60016 | powder | "Duck" outcrop | travertine forming now | 22.81464 | 57.83808 | ≈ 480 | 0.8159 | 0.0027 | 1,630 | 25 | -17.19 | trav | cc,dol,qtz,grn |
| OM07-26 | OS-60111 | fragments | settlment of Tuf | botryoidal carbonate weathering out of carb veins in serpentine | 23.105 | 57.957 | ≈ 900 | 0.0404 | 0.0006 | 25,800 | 130 | -7.78 | vein | |
| OM07-27 | OS-59339 | powder | settlment of Tuf | massive carbonate in wadi assoc w big (≤ 1 m) veins | 23.10807 | 57.95787 | 917 | 0.0041 | 0.0002 | 44,100 | 340 | -5.46 | vein | dol,serp,cct,grn,kao |

| Our sample no. | NOSAMS accession no. | Sample type | Location | Description | Latitude, °N | Longi- tude, °E | Eleva- tion, m | Fraction modern. C | Frac mod uncertainty | ¹⁴ C age, yrs | Age uncertainty, yrs | δ ¹³ C ‰, VPDB | Travertine or vein | Minerals most to least abundant, <10% <i>in italics</i> |
|----------------|-------------------------|-------------|-------------------------------|---|-----------------|--------------------|-------------------|-----------------------|-------------------------|-----------------------------|-------------------------|------------------------------|-----------------------|--|
| dup OM07-27 | OS-60020 | fragments | settlement of Tuf | massive carbonate in wadi | 23.10807 | 57.95787 | 917 | 0.0101 | 0.0003 | 36,900 | 270 | -6.28 | vein | <i>dol,serp,cct,grn,kao</i> |
| OM07-28C | OS-60077 | fragments | settlement of Tuf | low angle carbonate vein dipping 25-30° SW | 23.09935 | 57.95248 | 883 | 0.0515 | 0.0006 | 23,800 | 90 | -6.45 | vein | |
| OM07-30A | OS-60019 | powder | settlement of Tuf | travertine or dipslope vein in gully below Tuf | 23.09935 | 57.95248 | 883 | 0.0118 | 0.0003 | 35,600 | 220 | -7.34 | trav or vein | <i>dol,cct,serp,kao,grn</i> |
| OM07-30B | OS-60112 | powder | settlement of Tuf | dark grey limestone blocks within travertine or vein | 23.09935 | 57.95248 | 883 | 0.0845 | 0.0008 | 19,850 | 75 | 0.36 | trav | <i>cct,grn,serp,kao</i> |
| OM07-32 | OS-60116 | fragments | village of Falaij | carbonate veins in serpentized perid nr 34 | 22.84609 | 58.05617 | 551 | 0.3836 | 0.0018 | 7,700 | 35 | -7.39 | vein | |
| OM07-34A | OS-59333 | powder | village of Falaij | old travertine, 1.5 m above current spring level, big piece | 22.84609 | 58.05617 | 551 | 0.1367 | 0.0011 | 16,000 | 65 | -11.22 | trav | <i>cct,serp,dol</i> |
| dup OM07-34A | OS-60138 | fragments | village of Falaij | old travertine, 1.5 m above spring | 22.84609 | 58.05617 | 551 | 0.0742 | 0.0008 | 20,900 | 90 | -13.64 | trav | <i>cct,serp,dol</i> |
| OM07-34B | OS-60139 | fragments | village of Falaij | small carbonate vein in perid below travertine deposits | 22.84609 | 58.05617 | 551 | 0.4521 | 0.0019 | 6,380 | 35 | -6.3 | vein | |
| OM07-34C | OS-60113 | powder | village of Falaij | flakes of currently forming travertine | 22.84609 | 58.05617 | 551 | 1.1296 | 0.0043 | 0 | | -25.55 | trav | <i>cct,dol,kao,grn</i> |
| OM07-39 | OS-59336 | powder | Wadi Lufti | 50 cm carbonate vein in wadi wall | 23.24827 | 58.30994 | 600 | 0.0191 | 0.0003 | 31,800 | 140 | -8.39 | vein | <i>mag,dol,serp</i> |
| OM07-52 | OS-59998 | fragments | Wadi Nassif | serp & carb veins 5 cm thick in perid | 22.908 | 58.374 | ≈ 710 | 0.4146 | 0.0029 | 7,070 | 55 | -7.34 | vein | |
| OM07-53 | OS-60018 | powder | Wadi Nassif | carb vein in dunite, low angle dip | 22.908 | 58.374 | ≈ 710 | 0.0056 | 0.0002 | 41,700 | 340 | -8.1 | vein | |
| OM07-54 | OS-59334 | powder | pass betw W Khafifah & W Dima | carbonate coating/veins on joints | 22.93592 | 58.42621 | 748 | 0.0086 | 0.0003 | 38,200 | 300 | -2.78 | vein | <i>dol,serp,kao,grn</i> |
| OM07-56 | OS-60114 | fragments | pass betw W Khafifah & W Dima | coarse, green serpentine + carbonate vein 1 cm wide | 22.93592 | 58.42621 | 748 | 0.0358 | 0.0008 | 26,700 | 170 | -4.83 | vein | |
| OM07-57 | OS-60067 | fragments | pass betw W Khafifah & W Dima | mixed serpentine and carbonate, cm scale veins | 22.93592 | 58.42621 | 748 | 0.0052 | 0.0002 | 42,200 | 350 | -7.35 | vein | |
| OM07-58 | OS-60115 | fragments | pass betw W Khafifah & W Dima | perid with mm scale carbonate on joints | 22.94071 | 58.44178 | 915 | 0.2606 | 0.0014 | 10,800 | 40 | -4.34 | vein | |

| Our sample no. | NOSAMS accession no. | Sample type | Location | Description | Latitude, °N | Longitude, °E | Elevation, m | Fraction modern, C | Frac mod uncertainty | ¹⁴ C age, yrs | Age uncertainty, yrs | δ ¹³ C ‰, VPDB | Travertine or vein | Minerals most to least abundant, <10% in <i>italics</i> |
|----------------|----------------------|-------------|--------------------|--|--------------|---------------|--------------|--------------------|----------------------|--------------------------|----------------------|---------------------------|--------------------|---|
| OM07-59 | OS-59335 | powder | Wadi Dhuli | 4 mm carbonate chips in serpentine | 22.98407 | 58.63310 | 414 | 0.2221 | 0.0012 | 12,100 | 45 | -0.13 | vein | |
| dup OM07-59 | OS-60078 | fragments | Wadi Dhuli | 4 mm carb potato chips in serp | 22.98407 | 58.63310 | 414 | 0.1459 | 0.0013 | 15,450 | 70 | 1.59 | vein | |
| OM07-60 | OS-59340 | powder | nr ctr of universe | travertine or low angle vein grading into carbonated dunite | 22.93906 | 58.66805 | 497 | 0.0185 | 0.0004 | 32,000 | 170 | -11.91 | vein or trav | dol,mag, serp, <i>grn</i> |
| OM07-61A | OS-59341 | powder | Batin camp | erosional remnant of massive, low angle vein | 22.92564 | 58.67109 | 522 | 0.0275 | 0.0004 | 28,900 | 110 | -7.76 | vein | mag,dol |
| dup OM07-61A | OS-60075 | fragments | Batin camp | erosional remnant of massive, low angle vein | 22.92564 | 58.67109 | 522 | 0.0099 | 0.0004 | 37,000 | 340 | -8.35 | vein | mag,dol |
| OM07-61B | OS-60017 | powder | Batin camp | different textural types near top of spine leading SW from 61A | 22.92564 | 58.67109 | 522 | 0.1526 | 0.0012 | 15,100 | 65 | -0.88 | vein | |
| OM07-61C | OS-60079 | powder | Batin camp | different textural types near top of spine leading SW from 61A | 22.92564 | 58.67109 | 522 | 0.1123 | 0.0010 | 17,550 | 75 | -2.12 | vein | dol,mag, <i>grn,serp</i> |

Samples were analyzed for ¹⁴C age determination at the National Ocean Sciences Accelerator Mass Spectrometry Facility in Woods Hole, Massachusetts (NOSAMS). Samples were washed in dilute HCl and broken into ≈ 5 mm sized fragments, after which some were ground to powder in an agate mill, prior to shipment to NOSAMS. At NOSAMS, samples were directly hydrolyzed with strong acid, H₃PO₄, to convert the carbon in the sample to CO₂. Carbon dioxide was reacted with a catalyst to form graphite. An Fe/H₂ catalytic-reduction was used. Graphite was pressed into targets, which were analyzed on the accelerator along with standards and process blanks. Two primary standards were used during all ¹⁴C measurements: NBS Oxalic Acid I (NIST-SRM-4990) and Oxalic Acid II (NIST-SRM-4990C). The ¹⁴C activity ratio of Oxalic Acid II (δ¹³C = -17.3 per mil) to Oxalic Acid I (δ¹³C = -19.0 per mil) was taken to be 1.293. Every group of samples processed included a blank which was analyzed concurrently with the group. The process blank material was IAEA C-1 Carrera marble.

Fraction Modern (Fm) is a measurement of the deviation of the ¹⁴C/C ratio of a sample from "modern." Modern is defined as 95% of the radiocarbon concentration (in AD 1950) of NBS Oxalic Acid I normalized to δ¹³CVPDB = -19 per mil (Olsson, Nobel Symposium, 12th Proc., John Wiley & Sons, New York, p. 17, 1970). AMS results are calculated using the internationally accepted "modern value" of $1.176 \pm 0.010 \times 10^{-12}$ (Karlen et. al. Absolute determination of the activity of two ¹⁴C dating standards. Arkiv Geofysik 4, 465-471, 1968) and a final ¹³C correction is made to normalize the sample Fm to a δ¹³CVPDB value of -25 per mil. Stable isotope measurements of sample δ¹³C used to correct Fm values were made at the NOSAMS Facility by analyzing sub-samples of the CO₂ gas generated during graphite production with either a VG PRISM or VG OPTIMA mass spectrometer.

Reporting of ages and/or activities follows the convention outlined by Stuiver and Polach (Discussion: Reporting of ¹⁴C data. Radiocarbon, 19, 355-363, 1977) and Stuiver (Workshop on ¹⁴C data reporting. Radiocarbon, 22, 964, 1980). Radiocarbon ages are calculated using 5568 yrs as the half-life of radiocarbon and are reported without reservoir corrections or calibration to calendar years.

Atoms of ¹⁴C contained in a sample are directly counted using the AMS method of radiocarbon analysis, therefore, internal statistical uncertainty is calculated using the number of counts measured from each target. An external precision is calculated from the reproducibility of individual analyses for a given target. The uncertainty reported is the larger of the internal or external uncertainty.

Proportion of minerals was determined using a combination of X-Ray Fluorescence analyses for major element composition (Washington State University) and X-Ray Diffraction (at Woods Hole Oceanographic Institution, by Margaret Sulanowska) on powders, with data analysis using Mac-Diff software. Proportions were determined by Lisa Streit using least squares mass balance of the XRF data, beginning with the mineral identifications from XRD. Minerals listed are dolomite (dol), calcite (cct), magnesite (mag), chrysotile (serpentine polymorph, serp), quartz (qtz), greenalite (grn), and kaolinite (kao). Some of these mineral identifications are uncertain, so that other Mg-Ca carbonates such as huntite may be present instead of or in addition to dolomite + calcite, and serpentine polymorphs, clays and other hydrous silicates may be present instead of or in addition to greenalite and kaolinite. In preliminary electron microprobe analyses we have identified carbonates with Ca/Mg intermediate between calcite and dolomite, as reported for some veins and travertines in California (Barnes & O'Neil, Geochim. Cosmochim. Acta, 51, 699-713, 1951) and Oman (Stanger & Neal, Chem. Geol. 112, 247-254, 1994). Away from currently forming travertines, veins are dominantly dolomite and magnesite; within a few meters of currently forming travertines, veins contain abundant calcite ± dolomite; travertines are dominated by calcite.

Table S2. Transects of carbonate vein thickness in peridotite outcrops

| | Transect length, mm | Total vein thickness, mm | % veins | no. veins | UTM Zone 40Q | | Elevation, m |
|------------------------------------|---------------------|--------------------------|---------|-----------|--------------|---------|--------------|
| | | | | | UTM E | UTM N | |
| Far from active springs | | | | | | | |
| roadcutjohn1 | 29,171 | 229 | 0.79% | 25 | 647827 | 2537677 | 912 |
| roadcutjohn2 | 8,080 | 82 | 1.01% | 12 | 647827 | 2537677 | 912 |
| roadcutpeter1 | 10,040 | 22 | 0.22% | 43 | 647967 | 2537823 | 884 |
| roadcutpeter2 | 10,750 | 148.3 | 1.38% | 47 | 647942 | 2537818 | 902 |
| Totals | 58,041 | 481.3 | | 127 | | | |
| Length-weighted average proportion | | 0.83% | | | | | |
| Near springs | | | | | | | |
| duckgreg1 | 4,120 | 193 | 4.68% | 25 | 586213 | 2523342 | ≈520 |
| duckgreg2a | 1,110 | 122 | 10.99% | 19 | 586112 | 2523167 | ≈520 |
| duckgreg2b | 370 | 42 | 11.35% | 7 | 586112 | 2523167 | ≈520 |
| duckgreg3 | 3,950 | 216 | 5.47% | 54 | 586400 | 2523275 | ≈520 |
| duckpeter1 | 7,775 | 270.75 | 3.48% | 102 | 586383 | 2523255 | ≈520 |
| duckpeter2 | 745 | 88 | 11.81% | 24 | 586154 | 2523325 | ≈520 |
| spring1 | 3,219 | 190 | 5.90% | 76 | 530058 | 2542632 | ≈575 |
| spring2 | 2,524 | 104 | 4.12% | 49 | 530058 | 2542632 | ≈575 |
| Totals | 23,813 | 1225.75 | | 251 | | | |
| Length-weighted average proportion | | 5.15% | | | | | |