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Permanent storage of carbon dioxide in geological reservoirs by mineral carbonation

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Anthropogenic greenhouse-gas emissions continue to increase rapidly despite efforts aimed at curbing the release of such gases. One potentially long-term solution for offsetting these emissions is the capture and storage of carbon dioxide. In principle, fluid or gaseous carbon dioxide can be injected into the Earth's crust and locked up as carbonate minerals through chemical reactions with calcium and magnesium ions supplied by silicate minerals. This process can lead to near-permanent and secure sequestration, but its feasibility depends on the ease and vigour of the reactions. Laboratory studies as well as natural analogues indicate that the rate of carbonate mineral formation is much higher in host rocks that are rich in magnesium- and calcium-bearing minerals. Such rocks include, for example, basalts and magnesium-rich mantle rocks that have been emplaced on the continents. Carbonate mineral precipitation could quickly clog up existing voids, presenting a challenge to this approach. However, field and laboratory observations suggest that the stress induced by rapid precipitation may lead to fracturing and subsequent increase in pore space. Future work should rigorously test the feasibility of this approach by addressing reaction kinetics, the evolution of permeability and field-scale injection methods.

Atmospheric CO_2 concentration has increased from 280 ppm during pre-industrial times to 380 ppm today as a result of human input, and this is thought to be causing enhanced global warming and ocean acidification[1]. Between 2000 and 2005, global CO_2 emissions from burning fossil fuels averaged 26.4 Gt CO_2 yr^{-1}, at or above the highest rates predicted by the Intergovernmental Panel on Climate Change (IPCC)[2]. Stabilization of atmospheric CO_2 below 450 ppm requires a 30 to 85% net reduction in CO_2 emissions by 2050 (ref. 1). Owing to the continuing use of fossil fuels, CO_2 capture and storage should be a component of realistic plans to cap or reduce atmospheric CO_2 concentrations[3,4].

Geological formations, such as deep saline aquifers, have been proposed as repositories for anthropogenic CO_2 (refs 3,5,6). The long-term safety and permanence of storage will depend on physical and chemical controls within the storage reservoir. Injection of CO_2 modifies ambient formation waters, inducing fluid–rock reactions that may lead to the immobilization of injected CO_2 (ref. 3), or alternatively to increased permeability[7]. Thus, the permanence and safety of geological CO_2 storage will be determined by *in situ* fluid–rock reactions.

Carbon dioxide storage mechanisms

CO_2 is generally proposed to be injected at >800 m depth, where it is in a supercritical state[3]. Supercritical CO_2 is buoyant with respect to host rocks, and aqueous fluids at relevant temperatures and pressures. As a result, buoyant CO_2 fluid can migrate back to the surface[3]. Leakage of buoyant high-mobility CO_2 reduces long-term CO_2 storage, and could contaminate shallow-water resources if dissolved in groundwater[8]. However, various trapping mechanisms can immobilize the injected CO_2. Different trapping mechanisms that are active during different residence times in the reservoir are summarized in Box 1 (based on ref. 3).

As mineral trapping facilitates long-term storage of CO_2 in the form of carbonate minerals, and can provide extremely large storage capacity in certain geological settings, it is of special interest and will be discussed further.

Mineral trapping occurs in a series of reactions. Dissolution of CO_2 acidifies formation water through the following reaction:

$$CO_2(aq) + H_2O = H_2CO_3 = HCO_3^- + H^+ = CO_3^{2-} + 2H^+ \qquad (1)$$

CO_2 solubility decreases with increasing temperature and ionic strength of the formation water, and increases with increasing pressure[9]. Dissolved CO_2 will dissociate into bicarbonate and carbonate ions (reaction (1)) and, if divalent cations are in solution, will precipitate as carbonate minerals (reactions (2) and (3)).

$$(Ca,Mg,Fe)^{2+} + HCO_3^- = (Ca,Mg,Fe)CO_3 + H^+ \qquad (2)$$

$$(Ca,Mg,Fe)^{2+} + CO_3^{2-} = (Ca,Mg,Fe)CO_3 \qquad (3)$$

Reactions (1) and (2) generate H^+ ions and will not proceed as written unless these ions are also consumed. Further water–rock reactions, such as calcium plagioclase dissolution (reaction (4)), consume H^+ ions, driving reactions (1) and (2) to the right, and resulting in precipitation of carbonate minerals (reaction (3)):

$$CaAl_2Si_2O_8 + 2H^+ + H_2O = Ca^{2+} + Al_2Si_2O_5(OH)_4 \qquad (4)$$

Thus, in addition to temperature, pressure and salinity, dissolution of CO_2 into formation waters depends on buffering pH through fluid–rock reactions. CO_2 storage in pore space is optimized in host rocks with a high pH buffer capacity, determined by the mineralogy of the rocks. Generally, reactions with silicate minerals buffer pH decrease owing to reaction (1), enhancing both solubility trapping and mineral storage[10].

Aquifers containing 'basic' silicate minerals with a high proportion of Mg and Ca, such as olivine, serpentine, pyroxenes and plagioclase, have the greatest potential to fix CO_2 as carbonate minerals because they have a high molar proportion of divalent cations and they react rapidly to form carbonate minerals[11,12]. Deep aquifers in sedimentary basins are often considered the most promising CO_2 storage sites owing to their large storage capacity in pore space, relatively high permeability and geographic ubiquity. However, the dominant rocks in sedimentary basins are sandstone, siltstone, shale and limestone, which generally contain minor quantities of basic silicate minerals[11]. Xu *et al.*[11] simulated the mineral trapping potential of (1) glauconitic

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Box 1 | Carbon dioxide trapping mechanisms.

In geological reservoirs, CO_2 is trapped by physical and chemical mechanisms, which can result in long-term and secure storage.

Physical trapping: Initially, the principal CO_2 trapping mechanism is the presence of low-permeability cap rocks, such as shales and salt deposits. Stratigraphic traps are present where high porosity reservoir rocks are overlain by low-permeability cap rocks as a result of changes in the depositional environment during sedimentation. Structural traps include folds and faults. Folds may form closed domes or anticlines occupied by saline water, oil and gas, whereas faults can act either as a permeability barrier or as a preferential pathway for escape of fluid or gas.

Residual saturation trapping: Some injected CO_2 will be trapped by retention as a separate phase in pore space, sometimes forming isolated CO_2 'bubbles' within aqueous fluid[49].

Solubility trapping: Dissolution of CO_2 into formation water[5,6] creates CO_2-rich aqueous fluid that is slightly denser than CO_2-free formation water. Thus, solubility trapping eliminates the buoyancy that drives free CO_2 upwards with respect to aqueous fluid.

Mineral trapping: Dissolving CO_2 in water produces weak carbonic acid, which can react with carbonate or silicate minerals to form bicarbonate ions. Continued reaction combines bicarbonate ions with calcium, magnesium and iron dissolved from silicate minerals such as feldspars, olivine, pyroxenes or clays to form solid carbonates[6,11].

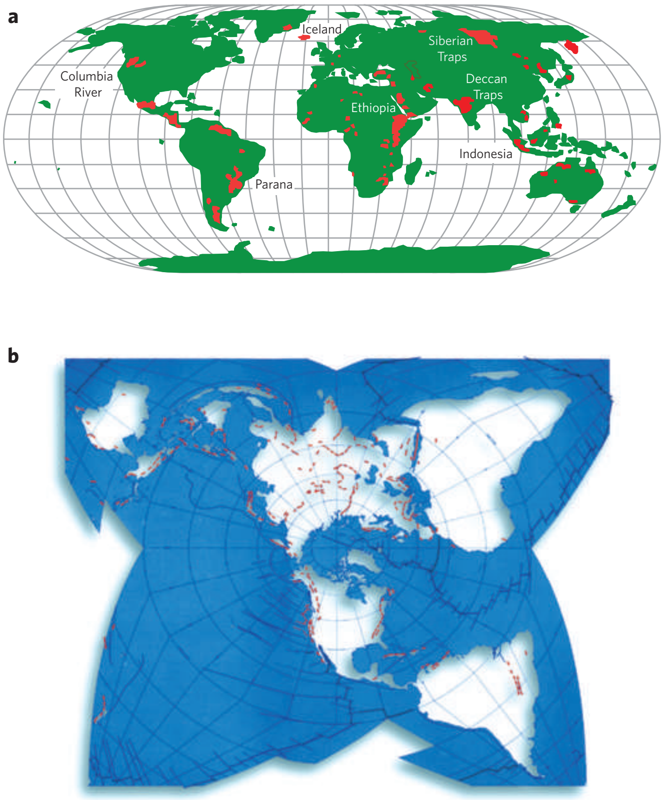

Figure 1 | Igneous rocks as carbon dioxide storage reservoirs. World map showing locations of continental basalt (**a**) and ophiolitic peridotite (**b**). Ophiolites are blocks of oceanic crust and upper mantle that have been exposed on land by tectonic forces. Part **a** taken from ref. 15 © 2008 MSA; part **b** taken from ref. 43 © 1998 WHOI after ref. 44.

sandstone (dominantly quartz, minor glauconite and illite) from the Alberta sedimentary basin in Canada, (2) US Gulf Coast sediments (dominantly quartz and plagioclase) and (3) a generic peridotite (olivine). An initial 1 M NaCl solution, used in all three simulations, reacted with the primary minerals at a constant CO_2 injection pressure of 260 bar and temperatures of 54 °C for glauconitic sandstone and 80 °C for the Gulf Coast sediments and peridotite. After 60,000 years, both glauconitic sandstone and Gulf Coast sediments are predicted to be almost completely carbonated, with a total CO_2 uptake of ~17 kg m^{-3} in glauconitic sandstone and ~90 kg m^{-3} in Gulf Coast sediments. After only 1,000 years, CO_2 uptake in peridotite is predicted to be ~100 kg m^{-3}. Xu *et al.* ended their simulation after 1,000 years assuming that precipitation of carbonate minerals in pore space would limit reaction progress. This assumption is not always valid (see below). Using rates from Xu *et al.*[11], complete carbonation of peridotite would take ~20,000 years, consuming ~2,000 kg CO_2 m^{-3} at a rate of 0.1 kg m^{-3} yr^{-1}, compared with 0.0015 kg m^{-3} yr^{-1} in Gulf Coast sediments.

Models predicting limited mineral carbonation in sedimentary rocks are complemented by field observations. A recent study of nine CO_2-rich natural gas reservoirs showed that the dominant sink for CO_2 is the dissolution of CO_2 in formation waters at pH 5–5.8, and that mineral carbonation is minor[13], due in part to the lack of basic silicate minerals. The impact of CO_2 storage on formation fluids and host rocks was also studied in the Frio-I brine pilot test in Texas[8], and in the Weyburn CO_2-injection site[14]. In Frio-I, dissolution of carbonate and iron oxyhydroxide minerals resulted in a significant increase in alkalinity and buffering of pH[8]. Owing to the lack of divalent cations in solution and/or the short duration of the experiments, no carbonate precipitation was observed. At Weyburn, dissolution of silicate minerals such as sodium and potassium feldspars enhanced aqueous CO_2 storage in the form of dissolved bicarbonate[14]. Reactions with alkali feldspars do not form carbonate minerals but produce bicarbonate-rich brines, buffering pH and increasing the mass of CO_2 stored through dissolution. Thus, clastic sedimentary rocks rich in alkalis have the capacity to buffer pH and to enhance CO_2 storage via solubility trapping[10]. However, where CO_2 mineral carbonation is important for permanent storage, host rocks rich in basic silicate minerals are preferred.

Unconventional storage reservoirs

Common, basic silicate minerals with the highest potential for CO_2 mineralization are olivine, pyroxenes, serpentine, plagioclase and basaltic glass[15]. These are primarily found in basalt and peridotite. Basalt forms the top igneous layer in oceanic crust, and occurs in large continental provinces, such as the Siberian Traps and the Columbia River Basalt Group (Fig. 1a). Ultramafic rocks such as peridotite are less abundant than basalt, but occur on almost every continent, with the largest volumes in the Sultanate of Oman, New Caledonia, Papua New Guinea and along the east coast of the Adriatic Sea. Numerous smaller peridotite bodies outcrop along the east and west coast of North America, with a combined volume similar to that in Oman (Fig. 1b).

McGrail *et al.*[16] showed that interbedded layers of brecciated and vesicular basalt within dense low-permeability units of the Columbia River Basalt Group may have the extent, permeability and porosity to support large-volume CO_2 storage. Estimated storage capacities in the Columbia River Basalt range from 36 to 148 billion tons[16]. Goldberg and Slagle[17] estimated storage capacities of 500–2,500 billion tons offshore from Washington and

British Columbia, and 1,000–5,500 billion tons in Caribbean flood basalts.

For total carbonation of peridotite within 5 km of the surface, uptake capacity is more than 30 trillion tons in Oman alone, and more than 100 trillion tons globally[18]. Total carbonation of such large volumes of peridotite is unlikely, but these values show that potential CO_2 storage in carbonated peridotite is enormous. Compared with basalt, ultramafic rocks such as peridotite probably have lower porosity and permeability, dominated by fissures in the weathered upper ~50 m and fractures in the deeper subsurface[19]. Permeability is likely to be scale-dependent owing to fracture size/frequency distributions. One study of groundwater flow[19] estimated the permeability of the fissured weathering horizon in mantle peridotite in Oman to be $\sim 10^{-14}$ m^2. Peridotite may have a permeability similar to other crystalline rocks in the upper crust, ranging from 10^{-13} to 10^{-10} m^2 for 1% fracture porosity measured over large scales at shallow depths[20], and 10^{-17} to 10^{-14} m^2 measured on smaller scales at greater depths[21]. As for some petroleum reservoirs, fractured ultramafic rocks could be excellent CO_2 storage reservoirs as long as fractured networks are overlain by a low-permeability cap.

Rates of *in situ* mineral carbonation in basalt and peridotite

Basalt and peridotite may provide permanent CO_2 storage by *in situ* mineral carbonation on the scale of billions of tons of CO_2 per year[16–18].

The potential for solid storage of CO_2 is demonstrated by natural analogues. Carbonation of basalt occurs through hydrothermal alteration, surface weathering and CO_2–water–rock reactions along groundwater flow paths, where divalent cations are released in solution and increase alkalinity[22–24]. As shown by Dessert *et al.*[24], natural carbonation of basalt consumes ~1.8 x 10^8 tons of CO_2 per year globally.

Natural carbonation of peridotite produces alkaline springs that form large travertine deposits, carbonate fracture and vein fillings[18,25–27] (Fig. 2), and carbonate chimneys at submarine hydrothermal vents[28]. CO_2 uptake by near surface carbonation is rapid; in Oman $\sim 10^3$ tons of CO_2 km^{-3} yr^{-1} are consumed by peridotite carbonation[18].

Natural uptake of CO_2 can be enhanced by a factor of $\sim 10^6$ through high-pressure injection of CO_2 into high-temperature peridotite. Peridotite contains 40–50 wt% MgO±CaO±FeO, compared with 20–25 wt% in basalt. Mg-rich compositions of the mineral olivine (Mg-end member, forsterite), which forms 60–95% of peridotite, dissolve and react more rapidly than the dominant compositional type of plagioclase (labradorite) that forms 50–70% of crystalline basalt (Fig. 3)[29].

Future studies may change this picture significantly, as inferred from the pace of recent discoveries. Experiments on crystalline basalt — mainly a mixture of ~60% plagioclase with 40% olivine + pyroxene — yielded rates higher than for plagioclase alone. Also, basalt glass dissolves 10 to 1,000 times faster than crystalline basalt and its primary constituent, labradorite[30]. In general, glass is not abundant because it is quickly hydrated and recrystallized during hydrothermal alteration and weathering. However, there may be some strata in which glass remains abundant. Overall, these new data on basalt and basaltic glass alteration rates indicate the need for continued kinetic studies, and for field characterization of proposed CO_2 reservoirs in basalt.

Notably, recent experiments in two different laboratories on carbonation of olivine to form magnesite + quartz in NaCl + $NaHCO_3$-rich or NaCl + $KHCO_3$-rich aqueous solutions at high pCO_2 and high olivine/fluid ratios show reaction rates 100 to 1,000 times faster than dissolution of olivine at the same pH but without high bicarbonate concentrations[31,32], despite the conventional assumptions that dissolution rates are highest at low concentrations, and that dissolution is rate limiting for carbonation reactions. These are the fastest known reaction rates for mafic silicate minerals reacting with H_2O–CO_2 fluids at 25–200 °C. Concentrated bicarbonate in CO_2-rich aqueous fluids may act as a catalyst, perhaps because it retards formation of silica reaction rims on olivine[31,32]. It is not clear how general this is, because experiments on basalt with high bicarbonate concentration have not been performed.

Carbonation and hydration of peridotite are exothermic. Rapid reaction at high temperature can enter a self-heating regime in which heat production is faster than cooling owing to injection of cold fluid and diffusive heat loss to cold surroundings[18]. The energy released by carbonation can then be used to maintain temperature at the optimal temperature for rapid reaction. For example, once a volume of peridotite at depth is above 125 °C, the reaction rate may be fast enough for heat production to exceed heat loss during injection of cold CO_2 at a rate of ~1 cm s^{-1}. Modulation of the flow rate can maintain high and nearly constant temperature without further energy input, and CO_2 uptake can exceed ~1 Gt km^{-3} yr^{-1}. The self-heating regime in basalt, if any, is probably at slower flow rates and higher temperature owing to slower reaction and smaller enthalpy changes.

Challenges for enhancing *in situ* mineral carbonation

Fluid–rock reactions that increase the solid volume, such as the carbonation of anhydrous silicates, are often self-limiting because they fill porosity, reduce permeability, and create ‘reaction rims’ that act as diffusive boundary layers between unreacted minerals and fluid, as proposed theorectically[33] and observed experimentally[34]. However, crystallization in pore space can also fracture rocks and increase permeability, for example when salt crystallizes from pore water in limestone[35]. MacDonald and Fyfe[36] proposed that increasing solid volume during olivine hydration produces stresses that fracture surrounding rock, as further investigated for weathering[37]. Reactive cracking may be likely during rapid mineral carbonation, and unlikely during slow carbonation. Increasing stress due to carbonate precipitation in pore space competes with

Figure 2 | Products of natural *in situ* mineral carbonation of peridotite. **a**, An actively depositing travertine terrace near the village of Falaji in Oman with altered peridotite in the background on the right side. Landcruiser for scale. **b**, Carbonate veins (white) in altered peridotite. Hammer for scale. **c**, A high alkaline spring with active precipitation of carbonate minerals in the Samail ophiolite near the village of Qafifah in Oman.

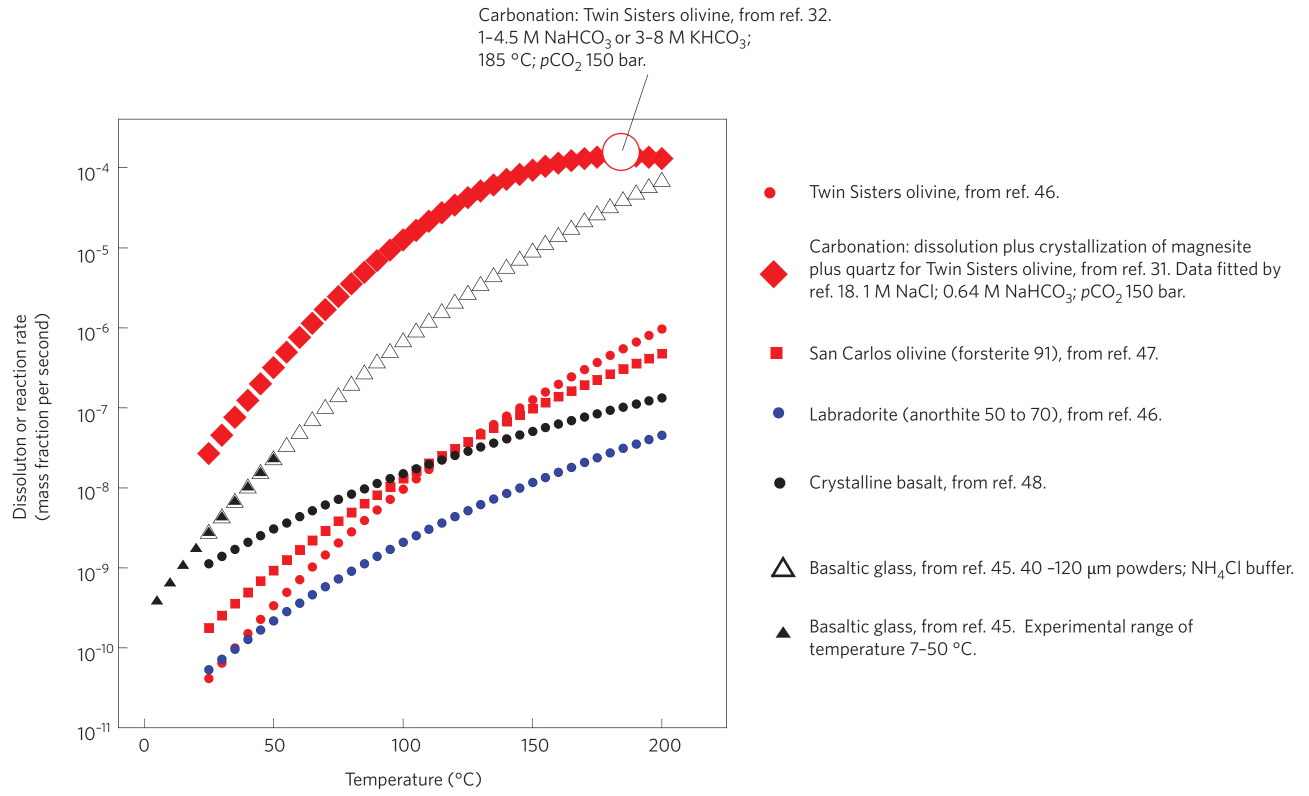

Figure 3 | Dissolution and carbonation rates. Compiled dissolution and carbonation rates of olivine, labradorite, crystalline basalt and basaltic glass are expressed in mass fraction per second as a function of temperature. Dissolution and carbonation rate data are from refs 31,32,45–48. Grain size ~70 μm; surface area ~spherical; pH ~8.

relaxation mechanisms such as viscous deformation of carbonate minerals. In analogue experiments, rapid crystallization of salt in pore space caused fractures whereas slow crystallization did not[38].

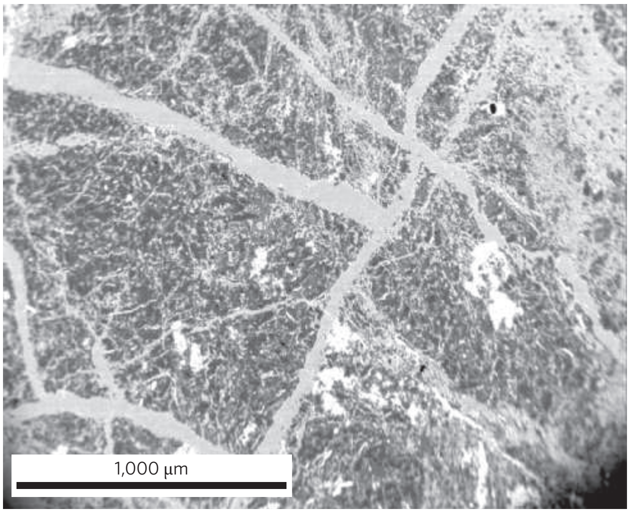

Figure 4 | Efficiency of peridotite carbonation. The backscattered electron microscope image shows a fully carbonated peridotite (listwanite) from the Sultanate of Oman, which is the result of *in situ* mineral carbonation. Dark areas are magnesium carbonate (magnesite), light grey areas are quartz and bright areas are relicts of the mineral chrome spinel. Photo by Lisa Streit (Columbia Univ.).

The idea that reaction-driven cracking can sustain permeability and reactive surface area is supported by numerous observations: extensive outcrops of completely carbonated peridotite (listwanite) show that natural carbonation is not always self-limiting[39]. Listwanites have brecciated textures in outcrops, and dense hierarchical fracture networks extending to microscopic scales, filled by syn-kinematic carbonate and quartz veins[18] (Fig. 4). Based on results from a recent geological study of carbonated serpentinites in Italy, Boschi *et al.*[40] concluded that a high fracture permeability was maintained by cyclic hydraulic fracturing during carbonation.

Laboratory experiments on carbonation of porous peridotite showed increasing permeability with time, even though the total solid volume increased by precipitation of magnesite, siderite and clay minerals[41]. Also, about 50% carbonation of peridotite in one locality occurred through reactions that consume hydrous minerals, rather than anhydrous olivine, producing a relatively small change in the solid volume[42].

To improve understanding of the linked chemical and physical processes that control mineral carbonation, further research is essential. This should include experiments to constrain combined dissolution and carbonation kinetics; experiments to constrain stress, fracture and permeability evolution during rapid carbonation; and pilot injection studies on a variety of scales. Two pilot studies to investigate *in situ* mineral carbonation in basaltic rocks are scheduled for the near future (www.carbfix.com; www.bigskyco2.org). A pilot study of enhanced mineral carbonation in Oman peridotite has been provisionally approved by the Directorate of Minerals in the Omani Ministry of Commerce and Industry and Petroleum Development Oman.

References

1. Solomon, S. *et al.* in *IPCC Climate Change 2007: The Physical Science Basis* (eds Solomon, S. *et al.*) 21–91 (Cambridge Univ. Press, 2007).
2. Leggett, J. A. & Logan, J. Are carbon dioxide emissions rising more rapidly than expected? *Congressional Research Service Report* RS22970 (2008).
3. IPCC *Special Report on Carbon Dioxide Capture and Storage* (eds Metz, B., Davidson, O., de Coninck, H. C., Loos, M. & Meyer, L. A.) 197–265 (Cambridge Univ. Press, 2005).
4. Schrag, D. Preparing to capture carbon. *Science* **315,** 812–813 (2007).
5. Gunter, W. D., Perkins, E. H. & McCann T. J. Aquifer disposal of CO_2-rich gases: reaction design for added capacity. *Energ. Convers. Manage.* **34,** 941–948 (1993).
6. Bachu, S., Gunter, W. D. & Perkins, E. H. Aquifer disposal of CO_2: hydrodynamic and mineral trapping. *Energ. Convers. Manage.* **35,** 269–279 (1994).
7. Gherardi, F., Xu, T. & Pruess, K. Numerical modeling of self-limiting and self-enhancing caprock alteration induced by CO_2 storage in a depleted gas reservoir. *Chem. Geol.* **244,** 103–129 (2007).
8. Kharaka, Y. K. *et al.* Gas-water-rock interactions in Frio Formation following CO_2 injection: Implications for the storage of greenhouse gases in sedimentary basins. *Geology* **34,** 577–580 (2006).
9. Portier, S. & Rochelle, C. Modelling CO_2 solubility in pure water and NaCl-type waters from 0 to 300 °C and from 1 to 300 bar. Application to the Utsira Formation at Sleipner. *Chem. Geol.* **217,** 187–199 (2005).
10. Gunter, W. D., Perkins, E. H. & Hutcheon, I. Aquifer disposal of acid gases: modeling of water-rock reactions for trapping of acid wastes. *Appl. Geochem.* **15,** 1085–1095 (2000).
11. Xu, T., Apps, J. A. & Pruess, K. Numerical simulation of CO_2 disposal by mineral trapping in deep aquifers. *Appl. Geochem.* **19,** 917–936 (2004).
12. Matter, J. M., Takahashi, T. & Goldberg, D. Experimental evaluation of *in situ* CO_2-water-rock reactions during CO_2 injection in basaltic rocks: Implications for geological CO_2 sequestration. *Geochem. Geophys. Geosyst.* **8,** Q02001 (2007).
13. Gilfillan, S. M. V. *et al.* Solubility trapping in formation water as dominant CO_2 sink in natural gas fields. *Nature* **458,** 614–618 (2009).
14. Raistrick, M. *et al.* Carbon dioxide-water-silicate mineral reactions enhance CO_2 storage; evidence from produced fluid measurements and geochemical modeling at the IEA Weyburn-Midale Project. *Energ. Procedia* **1,** 3149–3155 (2009).
15. Oelkers, E. H., Gislason, S. R. & Matter, J. Mineral carbonation of CO_2. *Elements* **4,** 333–337 (2008).
16. McGrail, B. P. *et al.* Potential for carbon dioxide sequestration in flood basalts. *J. Geophys. Res.* **111,** B12201 (2006).
17. Goldberg, D. & Slagle, A. L. A global assessment of deep-sea basalt sites for carbon sequestration. *Energ. Procedia* **1,** 3675–3682 (2009).
18. Kelemen, P. B. & Matter, J. *In situ* carbonation of peridotite for CO_2 storage. *Proc. Natl Acad. Sci.* **105,** 17295–17300 (2008).
19. Dewandel, B. *et al.* A conceptual hydrogeological model of ophiolite hard-rock aquifers in Oman based on a multiscale and a multidisciplinary approach. *Hydrogeol. J.* **13,** 708–726 (2005).
20. Wu, Y.-S., Zhang, K. & Liu, H.-H. Estimating large-scale fracture permeability of unsaturated rock using barometric pressure data. *Vadose Zone J.* **5,** 1129–1142 (2006).
21. Manning, C. E. & Ingebritsen, S. E. Permeability of the continental crust: implications of geothermal data and metamorphic systems. *Rev. Geophys.* **37,** 127–150 (1999).
22. Arnórsson, S. Deposition of calcium carbonate minerals from geothermal waters — theoretical considerations. *Geothermics* **18,** 33–40 (1989).
23. Gislason, S. R. & Eugster, H. P. Meteoric water-basalt interactions. II: A field study in N. E. Iceland. *Geochim. Cosmochim. Acta* **51,** 2841–2855 (1987).
24. Dessert, C., Dupré, B., Gaillardet, J., François, L. M. & Allègre, C. J. Basalt weathering laws and the impact of basalt weathering on the global carbon cycle. *Chem. Geol.* **202,** 257–273 (2003).
25. Barnes, I. & O'Neil, J. R. Relationship between fluids in some fresh alpine-type ultramafics and possible modern serpentinization, western United States. *Geol. Soc. Am. Bull.* **80,** 1947–1960 (1969).
26. Neal, C. & Stanger, G in *The Chemistry of Weathering* (ed. Drewer, J. I.) 249–275 (Reidel, 1985).
27. Cipolli, F., Gambardela, 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 CO_2 sequestration in serpentinite aquifers. *Appl. Geochem.* **19,** 787–802 (2004).
28. Kelley, D. S. *et al.* An off-axis hydrothermal vent field near the Mid-Atlantic ridge at 30° N. *Nature* **412,** 145–149 (2001).
29. Marini, L. *Geological Sequestration of Carbon Dioxide: Thermodynamics, Kinetics, and Reaction Path Modeling* (Elsevier, 2007).
30. Wolff-Boenisch, D., Gislason, S. R. & Oelkers, E. H. The effect of crystallinity on dissolution rates and CO_2 consumption capacity of silicates. *Geochim. Cosmochim. Acta* **70,** 858–870 (2006).
31. O'Connor, W. K., Dahlin, D. C., Rush, G. E., Gerdemann, S. J. & Nilsen, D. N. *Aqueous Mineral Carbonation: Final Report* DOE/ARC-TR-04-002 (US Department of Energy, 2004).
32. Chizmeshya, A. V. G., McKelvy M. J., Squires, K., Carpenter, R. W. & Béarat, H. A novel approach to mineral carbonation: Enhancing carbonation while avoiding mineral pretreatment process cost. *US Department of Energy Final Report* 924162 (Arizona State Univ., 2007).
33. Aharonov, E. Precipitation sealing and diagenesis – 2. Theoretical analysis. *J. Geophys. Res.* **103,** 23969–23981 (1998).
34. Tenthorey, E., Scholz, C. H., Aharonov, E. & Léger, A. Precipitation sealing and diagenesis – 1. Experimental results. *J. Geophys. Res.* **103,** 23951–23967 (1998).
35. Scherer, G. W. Crystallization in pores. *Cement Concrete Res.* **29,** 1347–1358 (1999).
36. MacDonald, A. H. & Fyfe, W. S. Rate of serpentinization in seafloor environments. *Tectonophysics* **116,** 123–135 (1985).
37. 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).
38. Liteanu, E. & Spiers, C. J. Influence of pore salt content on compaction creep of calcite aggregates in the presence of supercritical CO_2. *Chem. Geol.* **265,** 134–147 (2009).
39. Nasir, S. *et al.* Mineralogical and geochemical characterization of listwaenite from the Se-mail Ophiolite, Oman. *Chemie der Erde* **67,** 213–228 (2007).
40. Boschi, C., Dini, A., Dallai, L., Ruggieri, G. & Gianelli, G. Enhanced CO_2-mineral sequestration by cyclic hydraulic fracturing and Si-rich fluid infiltration into serpentinites at Malentrata (Tuscany, Italy). *Chem. Geol.* **265,** 209–226 (2009).
41. Andreani, M. *et al.* Experimental study of carbon sequestration reactions controlled by the percolation of CO_2-rich brine through peridotites. *Environ. Sci. Technol.* **43,** 1226–1231 (2009).
42. Hansen, L. D., Dipple, G. M., Gordon, T. M. & Kellett, D. A. Carbonated serpentinite (listwanite) at Alin, British Columbia: a geological analogue to carbon dioxide sequestration. *Can. Mineral.* **43,** 225–239 (2005).
43. Kelemen, P. Melt extraction from the mantle beneath mid-ocean ridges. *Oceanus* **41,** 23–28 (1998).
44. Coleman, R. G. *Ophiolites: Ancient Oceanic Lithosphere?* (Springer, 1977).
45. Gislason, S. R. & Oelkers, E. H. Mechanism, rates and consequences of basaltic glass dissolution: II. An experimental study of the dissolution rates of basaltic glass as a function of pH and temperature. *Geochim. Cosmochim. Acta* **67,** 3817–3832 (2003).
46. Palandri, J. L. & Kharaka, Y. K. A compilation of rate parameters of water-mineral interaction kinetics for application to geochemical modeling. *US Geological Survey Open File Report* 2004-1068 (2004).
47. Hänchen, M., Prigiobbe, V., Storti, G., Seward, T. M. & Mazzotti, M. Dissolution kinetics of fosteritic olivine at 90–150 °C including effects of the presence of CO_2. *Geochim. Cosmochim. Acta* **70,** 4403–4416 (2006).
48. Schaef, H. T. & McGrail, B. P. Dissolution of Columbia River Basalt under mildly acidic conditions as a function of temperature: Experimental results relevant to the geological sequestration of carbon dioxide. *Appl. Geochem.* **24,** 980–987 (2008).
49. Ide, T. S., Jessen, K. & Orr, F. M. Jr Storage of CO_2 in saline aquifers: effects of gravity, viscous, and capillary forces on amount and timing of trapping. *Int. J. Greenh. Gas Con.* **1,** 481–491 (2007).

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Author contributions

J.M.M. and P.B.K. jointly performed the data analysis and wrote the paper.