

# Permanent storage of carbon dioxide in geological reservoirs by mineral carbonation

Jürg M. Matter\* and Peter B. Kelemen

**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<sub>2</sub> 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<sup>1</sup>. Between 2000 and 2005, global CO<sub>2</sub> emissions from burning fossil fuels averaged 26.4 Gt CO<sub>2</sub> yr<sup>-1</sup>, at or above the highest rates predicted by the Intergovernmental Panel on Climate Change (IPCC)<sup>2</sup>. Stabilization of atmospheric CO<sub>2</sub> below 450 ppm requires a 30 to 85% net reduction in CO<sub>2</sub> emissions by 2050 (ref. 1). Owing to the continuing use of fossil fuels, CO<sub>2</sub> capture and storage should be a component of realistic plans to cap or reduce atmospheric CO<sub>2</sub> concentrations<sup>3,4</sup>.

Geological formations, such as deep saline aquifers, have been proposed as repositories for anthropogenic CO<sub>2</sub> (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<sub>2</sub> modifies ambient formation waters, inducing fluid–rock reactions that may lead to the immobilization of injected CO<sub>2</sub> (ref. 3), or alternatively to increased permeability<sup>7</sup>. Thus, the permanence and safety of geological CO<sub>2</sub> storage will be determined by *in situ* fluid–rock reactions.

## Carbon dioxide storage mechanisms

CO<sub>2</sub> is generally proposed to be injected at >800 m depth, where it is in a supercritical state<sup>3</sup>. Supercritical CO<sub>2</sub> is buoyant with respect to host rocks, and aqueous fluids at relevant temperatures and pressures. As a result, buoyant CO<sub>2</sub> fluid can migrate back to the surface<sup>3</sup>. Leakage of buoyant high-mobility CO<sub>2</sub> reduces long-term CO<sub>2</sub> storage, and could contaminate shallow-water resources if dissolved in groundwater<sup>8</sup>. However, various trapping mechanisms can immobilize the injected CO<sub>2</sub>. 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<sub>2</sub> 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<sub>2</sub> acidifies formation water through the following reaction:



CO<sub>2</sub> solubility decreases with increasing temperature and ionic strength of the formation water, and increases with increasing pressure<sup>9</sup>. Dissolved CO<sub>2</sub> 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)).



Reactions (1) and (2) generate H<sup>+</sup> 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<sup>+</sup> ions, driving reactions (1) and (2) to the right, and resulting in precipitation of carbonate minerals (reaction (3)):



Thus, in addition to temperature, pressure and salinity, dissolution of CO<sub>2</sub> into formation waters depends on buffering pH through fluid–rock reactions. CO<sub>2</sub> 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<sup>10</sup>.

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<sub>2</sub> as carbonate minerals because they have a high molar proportion of divalent cations and they react rapidly to form carbonate minerals<sup>11,12</sup>. Deep aquifers in sedimentary basins are often considered the most promising CO<sub>2</sub> 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<sup>11</sup>. Xu *et al.*<sup>11</sup> simulated the mineral trapping potential of (1) glauconitic sandstone (dominantly quartz,



### Box 1 | Carbon dioxide trapping mechanisms.

In geological reservoirs, CO<sub>2</sub> is trapped by physical and chemical mechanisms, which can result in long-term and secure storage.

**Physical trapping:** Initially, the principal CO<sub>2</sub> 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.

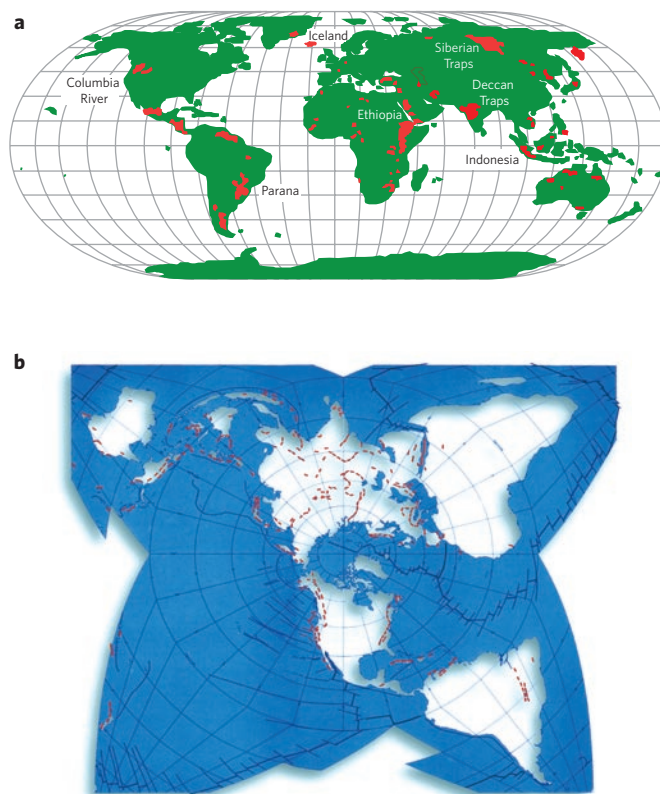
**Residual saturation trapping:** Some injected CO<sub>2</sub> will be trapped by retention as a separate phase in pore space, sometimes forming isolated CO<sub>2</sub> 'bubbles' within aqueous fluid<sup>49</sup>.

**Solubility trapping:** Dissolution of CO<sub>2</sub> into formation water<sup>5,6</sup> creates CO<sub>2</sub>-rich aqueous fluid that is slightly denser than CO<sub>2</sub>-free formation water. Thus, solubility trapping eliminates the buoyancy that drives free CO<sub>2</sub> upwards with respect to aqueous fluid.

**Mineral trapping:** Dissolving CO<sub>2</sub> 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<sup>6,11</sup>.

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<sub>2</sub> 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<sub>2</sub> uptake of ~17 kg m<sup>-3</sup> in glauconitic sandstone and ~90 kg m<sup>-3</sup> in Gulf Coast sediments. After only 1,000 years, CO<sub>2</sub> uptake in peridotite is predicted to be ~100 kg m<sup>-3</sup>. 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.*<sup>11</sup>, complete carbonation of peridotite would take ~20,000 years, consuming ~2,000 kg CO<sub>2</sub> m<sup>-3</sup> at a rate of 0.1 kg m<sup>-3</sup> yr<sup>-1</sup>, compared with 0.0015 kg m<sup>-3</sup> yr<sup>-1</sup> in Gulf Coast sediments.

Models predicting limited mineral carbonation in sedimentary rocks are complemented by field observations. A recent study of nine CO<sub>2</sub>-rich natural gas reservoirs showed that the dominant sink for CO<sub>2</sub> is the dissolution of CO<sub>2</sub> in formation waters at pH 5–5.8, and that mineral carbonation is minor<sup>13</sup>, due in part to the lack of basic silicate minerals. The impact of CO<sub>2</sub> storage on formation fluids and host rocks was also studied in the Frio-I brine pilot test in Texas<sup>8</sup>, and in the Weyburn CO<sub>2</sub>-injection site<sup>14</sup>. In Frio-I, dissolution of carbonate and iron oxyhydroxide minerals resulted in a significant increase in alkalinity and buffering of pH<sup>8</sup>. 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



**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.

feldspars enhanced aqueous CO<sub>2</sub> storage in the form of dissolved bicarbonate<sup>14</sup>. Reactions with alkali feldspars do not form carbonate minerals but produce bicarbonate-rich brines, buffering pH and increasing the mass of CO<sub>2</sub> stored through dissolution. Thus, clastic sedimentary rocks rich in alkalis have the capacity to buffer pH and to enhance CO<sub>2</sub> storage via solubility trapping<sup>10</sup>. However, where CO<sub>2</sub> 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<sub>2</sub> mineralization are olivine, pyroxenes, serpentine, plagioclase and basaltic glass<sup>15</sup>. 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.*<sup>16</sup> 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<sub>2</sub> storage. Estimated storage capacities in the Columbia River Basalt range from 36 to 148 billion tons<sup>16</sup>. Goldberg and Slagle<sup>17</sup> 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<sup>18</sup>. Total carbonation of such large volumes of peridotite is unlikely, but these values show that potential CO<sub>2</sub> 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<sup>19</sup>. Permeability is likely to be scale-dependent owing to fracture size/frequency distributions. One study of groundwater flow<sup>19</sup> estimated the permeability of the fissured weathering horizon in mantle peridotite in Oman to be ~10<sup>-14</sup> m<sup>2</sup>. Peridotite may have a permeability similar to other crystalline rocks in the upper crust, ranging from 10<sup>-13</sup> to 10<sup>-10</sup> m<sup>2</sup> for 1% fracture porosity measured over large scales at shallow depths<sup>20</sup>, and 10<sup>-17</sup> to 10<sup>-14</sup> m<sup>2</sup> measured on smaller scales at greater depths<sup>21</sup>. As for some petroleum reservoirs, fractured ultramafic rocks could be excellent CO<sub>2</sub> 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<sub>2</sub> storage by *in situ* mineral carbonation on the scale of billions of tons of CO<sub>2</sub> per year<sup>16–18</sup>.

The potential for solid storage of CO<sub>2</sub> is demonstrated by natural analogues. Carbonation of basalt occurs through hydrothermal alteration, surface weathering and CO<sub>2</sub>–water–rock reactions along groundwater flow paths, where divalent cations are released in solution and increase alkalinity<sup>22–24</sup>. As shown by Dessert *et al.*<sup>24</sup>, natural carbonation of basalt consumes ~1.8 × 10<sup>8</sup> tons of CO<sub>2</sub> per year globally.

Natural carbonation of peridotite produces alkaline springs that form large travertine deposits, carbonate fracture and vein fillings<sup>18,25–27</sup> (Fig. 2), and carbonate chimneys at submarine hydrothermal vents<sup>28</sup>. CO<sub>2</sub> uptake by near surface carbonation is rapid; in Oman ~10<sup>3</sup> tons of CO<sub>2</sub> km<sup>-3</sup> yr<sup>-1</sup> are consumed by peridotite carbonation<sup>18</sup>.

Natural uptake of CO<sub>2</sub> can be enhanced by a factor of ~10<sup>6</sup> through high-pressure injection of CO<sub>2</sub> 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)<sup>29</sup>.

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<sup>30</sup>. 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<sub>2</sub> reservoirs in basalt.

Notably, recent experiments in two different laboratories on carbonation of olivine to form magnesite + quartz in NaCl + NaHCO<sub>3</sub>-rich or NaCl + KHCO<sub>3</sub>-rich aqueous solutions at high *p*CO<sub>2</sub> 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<sup>31,32</sup>, 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<sub>2</sub>O–CO<sub>2</sub> fluids at 25–200 °C. Concentrated bicarbonate in CO<sub>2</sub>-rich aqueous fluids may act as a catalyst, perhaps because it retards formation of silica reaction rims on olivine<sup>31,32</sup>. 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<sup>18</sup>. 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<sub>2</sub> at a rate of ~1 cm s<sup>-1</sup>. Modulation of the flow rate can maintain high and nearly constant temperature without further energy input, and CO<sub>2</sub> uptake can exceed ~1 Gt km<sup>-3</sup> yr<sup>-1</sup>. 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

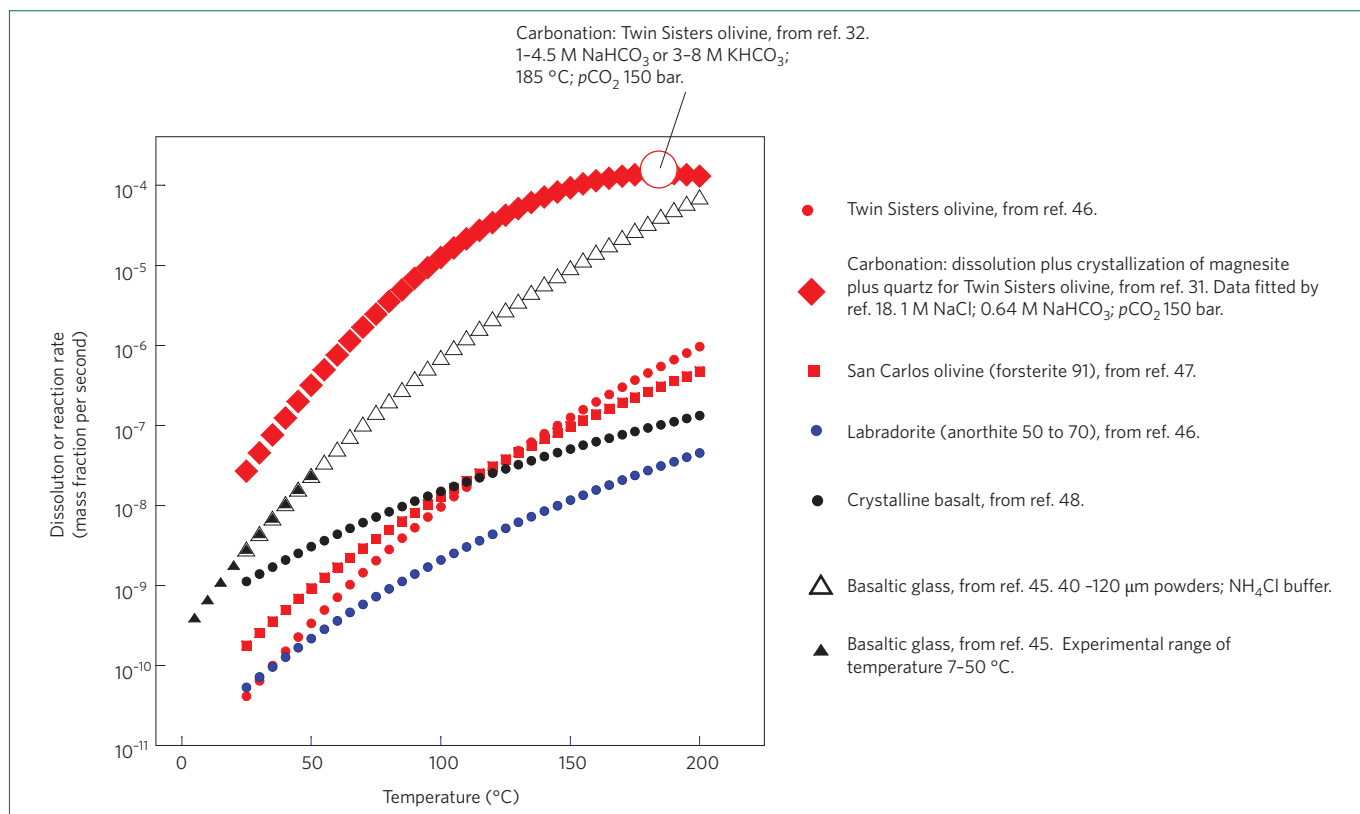
Fluid–rock reactions that increase the solid volume, such as the carbonation of anhydrous silicates, are often self-limiting because they fill porosity, reduce permeability, and create ‘reaction rims’ that act as diffusive boundary layers between unreacted minerals and fluid, as proposed theoretically<sup>33</sup> and observed experimentally<sup>34</sup>. However, crystallization in pore space can also fracture rocks and increase permeability, for example when salt crystallizes from pore water in limestone<sup>35</sup>. MacDonald and Fyfe<sup>36</sup> proposed that increasing solid volume during olivine hydration produces stresses that fracture surrounding rock, as further investigated for weathering<sup>37</sup>. 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.**

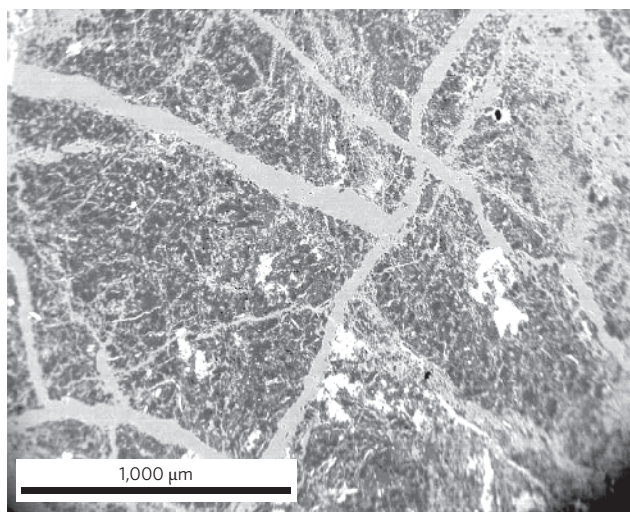
**a**, An actively depositing travertine terrace near the village of Falaji in Oman with altered peridotite in the background on the right side. Landcruiser for scale. **b**, Carbonate veins (white) in altered peridotite. Hammer for scale. **c**, A high alkaline spring with active precipitation of carbonate 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  $\sim 70 \mu\text{m}$ ; surface area  $\sim$ spherical; pH  $\sim 8$ .

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<sup>38</sup>.



**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<sup>39</sup>. Listwanites have brecciated textures in outcrops, and dense hierarchical fracture networks extending to microscopic scales, filled by syn-kinematic carbonate and quartz veins<sup>18</sup> (Fig. 4). Based on results from a recent geological study of carbonated serpentinites in Italy, Boschi *et al.*<sup>40</sup> 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<sup>41</sup>. 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<sup>42</sup>.

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](http://www.carbfix.com); [www.bigskyco2.org](http://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.



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## Author contributions

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