Rapid mineralisation of carbon dioxide in peridotites

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Abstract

The success of industrial scale carbon capture and storage in geologic reservoirs depends on the permanence of the stored carbon dioxide (CO_2). Carbon dioxide capture and mineralisation (CCM) or mineral carbonation, which is the conversion of CO_2 to carbonate minerals via fluid-rock reactions provides low risk and permanent CO_2 removal. Here, we demonstrate rapid mineralisation of industrial CO_2 emissions in mantle peridotites. Captured CO_2 from an ammonia plant in the Sultanate of Oman has been injected into peridotite at a pilot test site in the Samail ophiolite. Chemical and isotopic results indicate rapid carbonate mineral precipitation. Mass balance calculations suggest that ~88% of the injected CO_2 was mineralised as carbonate minerals within 45 days after injection. This successful approach of CCM unlocks peridotite as a promising new type of reservoir for the safe and permanent disposal of anthropogenic CO_2 emissions.

Introduction

Cumulative carbon dioxide emissions into the atmosphere have been estimated at 2,035 ± 205 $GtCO_2$ from 1870 to 2019[1]. To limit the impact of global warming and subsequent climate change, the Paris agreement recommended to limit average warming of the atmosphere to <2°C, preferably to 1.5° compared to pre-industrial levels[1]. To reach this goal, the level of global carbon dioxide removal coupled with permanent storage must be approximately 10 Gt CO_2/yr by 2050 and 20 Gt CO_2/yr by 2100[2]. There are multiple storage options, with underground CO_2 storage in sedimentary formations being the most mature technique, with over 200 Mt of anthropogenic CO_2 being injected and stored in underground reservoirs for enhanced oil recovery by today[3]. Current estimates of aggregated global storage resources in underground reservoirs (mainly deep saline aquifers and depleted oil & gas reservoirs) are 13,954 $GtCO_2$[4]. In this type of reservoirs, CO_2 is primarily stored as supercritical or liquid CO_2, with the tendency to migrate back to the surface due to buoyancy effects if not stored adequately. Another storage option is enhanced CO_2 mineralisation in unconventional storage reservoirs, such as basalt and peridotite that mimics the natural process of silicate rock weathering[5-12]. In this approach, injected CO_2 reacts with mafic and ultramafic rocks, which contain high concentrations of calcium, magnesium, and iron, required for CO_2 mineralisation. Combining CO_2 dissolution into water before or during the injection with in-situ CO_2 mineralisation significantly increases storage permanence and security by immediate solubility trapping and subsequent mineralisation[13,14,15].

In-situ mineralisation in basalt has been successfully tested in a first pilot project in Iceland in 2012[16]. A total of 230 tonnes of pure CO_2 and a CO_2-H_2S mixture were injected fully dissolved in water into a basalt reservoir at 500 m depth[16]. Co-injection of non-reactive and reactive tracers, combined with detailed geochemical analysis of produced reservoir waters before, during and after the injection revealed rapid mineralisation of >95% of the injected CO_2 within less than two years[17,18,19]. This storage technique has been further developed and implemented to a commercial scale by CarbFix, with > 84 thousand tonnes of CO_2 injected since 2014[20]. Theoretical global mineralisation potential in onshore and offshore basalt are on the order of several 100,000 $GtCO_2$ with a capacity of ~170 kg CO_2 per ton of basalt[5,7,21,22,23].

Ultramafic rocks, such as peridotites, provide the other main storage reservoir for in-situ mineralisation. Peridotites have a higher molar Mg to Si ratio and faster reaction kinetics with CO_2-saturated fluids than basalt, making them an ideal candidate for mineralisation[24-29]. Peridotite is a major component of the Earth's upper mantle and is exposed in several large ophiolite massifs, such the Samail ophiolite in Oman and the United Arab Emirates. It is mainly composed of the minerals olivine, serpentine and brucite, which rapidly react with water containing CO_2. Extensive natural CO_2 mineralisation has been observed in the Samail ophiolite with rates on the order of 1,000 $tCO_2/km^3/yr$[6,25]. Recent studies showed that natural carbon mineralisation through weathering and groundwater circulation is limited to the upper tens of meters in the peridotite, with the deeper subsurface being CO_2 depleted[29]. Due to the disequilibrium of peridotite with atmospheric CO_2 and CO_2-saturated water below ~100 m depth, peridotites provide a large mineralisation reservoir with a theoretical mineralisation potential of 10^5-10^8 $GtCO_2$ in Oman alone, and a capacity of 500-600 kg CO_2 per ton of peridotite[6,25].

To date, engineered CO_2 mineralisation in peridotite has not been tested on a pilot scale. In this study, we use chemical and isotopic data from Project Chalk, the world's first in-situ CO_2 mineralisation pilot in peridotites in the Samail ophiolite, Oman, to constrain the reaction kinetics of in-situ CO_2-water-rock reactions resulting in permanent CO_2 mineralisation.

Results

Test site

The Oman Drilling Project (OmanDP) drilled multiple boreholes at the Oman Drilling Project Multi-borehole Observatory (MBO) in Wadi Lawayni, in the Tayin massif of the Oman ophiolite, approximately 25 km NE of Ibra, Oman (Fig. 1). The boreholes were drilled and fully characterized using wireline geophysical logging and hydrogeological testing by the Oman Drilling Project[30,31]. Core and drill cutting analysis indicate serpentinized dunite in the upper 100-250 m, and partially serpentinized harzburgite in the deeper part, with both rock types showing high density of mineralised veins[29]. Visual core description of continuous cores from boreholes BA1B and BA4A reveal that waxy green to white serpentines are the dominant vein minerals, whereas Ca-Mg carbonate filled veins are only found in the shallow part of the subsurface (<100 m)[29]. Borehole pumping tests using a straddle packer system revealed distinct zones of higher permeability with hydraulic conductivity values between 1.6×10^{-2} m/s (41-65 m below ground level interval, mbgl), 2.5×10^{-6} m/s (108-135 mbgl), and $<2.3 \times 10^{-8}$ m/s (135 – 400 mbgl)[31]. Wireline logging and discrete fluid sampling indicated a stratification of the aquifer in well BA1A with oxidized, pH ~8 and electrical conductivity of ~580 µS/cm fluids in the upper 65-150 m, and highly reduced, pH >10, and electrical conductivity of ~1800 µS/cm fluids below 150 m depth[30,32]. No such stratification occurs in well BA1D, which is ~16 m apart from BA1A, revealing the heterogeneity of the peridotite[32]. Groundwater in BA1D is highly reduced with a pH >10 and an electrical conductivity of 1720 µS/cm[32].

For the Project Chalk B, we utilized one of the existing 400-meter-deep boreholes, BA1D, for a single-well ('huff-n-puff) push-pull tests (Fig. 1).

'Pull solution' chemical and isotopic results

We report the pre-injection chemical and isotopic composition of the groundwater (GW) and the injected solution (IS) in Table 1. GW represents the ambient groundwater in the target injection interval, and the IS water is shallow groundwater, which was pumped prior to the injection and stored in a surface tank. We also report chemical and isotopic data from a post-injection time series of 'pull-solution' samples collected in well BA1D (Table S2). The pre-injection groundwater in the isolate interval had a pH of 11.02, a Br^- tracer concentration below detection limit, and the dissolved inorganic carbon (DIC = dissolved CO_2 + HCO_3^- + CO_3^{2-}) was 154.8 μmol/L, whereas the injected solution had a pH of 4.1, a Br- tracer concentration of 4.42 mmol/L, and a DIC concentration of 122.3 mol/L (Table 1). Stable carbon isotope ratio of the DIC ($\delta^{13}C_{DIC}$) of GW and IS were -20.10 and -33.50‰ V-PDB, respectively (Table 1).

The pH in the reservoir at the beginning of the pull phase was 7.45 but steadily increasing to 9.50 with increasing pumping time (Table S2). The chemical and isotopic composition of the extracted 'pull-solution' (Ca^{2+}, Mg^{2+}, Na^+, ΣSi, DIC and $\delta^{13}C_{DIC}$) evolved during the pull phase (Table S2). Bromide decreased from 0.72 mmol/L at the beginning of the pumping to between 0.11 and 0.12 mmol/L due to mixing of the injected solution with the groundwater ('solution mixing') in the reservoir (Fig. 2). The total recovery of Br^- was 37.61% as estimated by dividing the mass of bromide recovered during the pull phase by the mass of bromide injected. Calcium concentration displayed a sharp increase from 0.55 to 2.01 mmol/L, whereas Mg^{2+} concentration decreased from 2.64 to 0.08 mmol/L, almost reaching pre-injection groundwater concentration of 0.002 mmol/L (Fig. 3). Sodium concentration generally increased from 2.91 to 5.04 mmol/L (Fig. 3). Total dissolved silicon concentration (ΣSi) in the collected 'pull solution' samples, initially increased from 0.58 to 0.66 mmol/L but subsequently decreased to 0.43 mmol/L, whereas measured DIC concentrations decreased from 6.37 to 0.084 mmol/l (Fig. 3). These trends indicate that other processes in addition to conservative 'solution mixing' between the injected fluid and the groundwater occurred following the injection of the CO_2-saturated solution.

Host rock dissolution and mineral carbonation

The chemical and isotopic composition of the collected 'pull solution' samples from the injection reservoir indicate mixing and CO_2-water-rock reaction processes. To differentiate between mixing and water-rock reaction processes occurring in the reservoir post-injection, we first determined the concentrations of dissolved ions of interest, assuming non-reactive solution-mixing. The mixing ratio of the groundwater and injected solution was determined using the measured concentration of bromide, the injected non-reactive tracer (Table S2). Subsequently, mass balance calculations were used (Eqs. 1 – 2) to calculate the impact of non-reactive solution-mixing on the concentration of major dissolved ions (Table S3, Fig. 3). Differences between the measured and the predicted concentrations (Eq. 3) of these ions either suggest net dissolution (positive values) or net precipitation (negative values) (Table S4).

Measured Mg and ΣSi concentrations were higher than the predicted ones during the pull phase, indicating an input of these elements via dissolution of the host rock. Measured Ca, Na and DIC concentrations were significantly lower than the ones predicted assuming non-reactive mixing, suggesting net-precipitation of secondary minerals (Fig. 3).

Mineral saturation states

Saturation indices (SI) of the collected fluid samples with respect to primary and secondary minerals are shown in Fig. 4 and 5. Primary silicate minerals present in the peridotite, such as forsterite and pyroxene (e.g. enstatite) were consistently undersaturated (Fig 4). Various secondary silicate minerals from previous alteration (serpentine (chrysotile), brucite, chalcedony) show variable saturation states. Brucite was consistently undersaturated, whereas chrysotile was undersaturated at the beginning of the pull phase and oversaturated for the remaining pumping time. Chalcedony was close to saturation during the entire monitoring period. Key secondary minerals regarding CO_2 mineralisation, such as calcite and dolomite were at saturation or at supersaturation, whereas magnesite and hydromagnesite were undersaturated (Fig. 5).

Discussion

The evolution of the concentration of major elements, such as Ca, Mg, Na, Si as well as DIC reveal the effect of the CO_2 reactivity. Differences between the measured and the calculated concentrations that assume non-reactive mixing, reveal mineral dissolution and precipitation reactions. Increasing Mg and ΣSi concentrations with positive computed ΔMg and ΔSi values suggest a net input of these elements by dissolution of the host rock (Table S4). Measured ΣSi concentrations initially increased and then slightly decreased but stayed higher than the predicted one for the whole duration of the pull phase, whereas the measured Mg concentration decreased during the pull phase but never reached the calculated concentration for non-reactive solution-mixing. Measured concentrations of Ca, Na and DIC decreased with increasing pumping time but were always below the calculated concentrations assuming non-reactive solution-mixing, as revealed by the negative ΔCa, ΔDIC, ΔNa, which indicate precipitation of secondary minerals (Table S4).

Fate of injected CO_2

The chemical and isotopic composition of the extracted water samples reveal the reactivity of the injected CO_2-saturated solution within the reservoir. Bromide was co-injected as a conservative, non-reactive tracer, and its volume integrated amounts recovered by pumping indicate a tracer recovery rate of 37.6%, meaning that we lost ~62% of Br (i.e. injected solution) through dispersion in the reservoir. Computed negative ΔCa, ΔDIC, ΔNa values indicate precipitation, whereas positive ΔMg and ΔSi values reveal dissolution reactions (Table S4). The fate of the injected CO_2 is demonstrated by the DIC mass balance. The injected mass of DIC was 1011 moles and the amount of re-pumped DIC corrected for the dispersion within the reservoir using the Br recovery rate of 37.6% was 120 moles. Thus, 891 moles of DIC (88%) were lost by reaction processes during the 45 days of incubation time, confirming the non-conservative behaviour of DIC in the reservoir. Reaction processes, such as degassing of dissolved CO_2, carbonate mineral dissolution or carbonate precipitation can change the total mass of inorganic carbon in the reservoir. Degassing of dissolved CO_2 from the injection reservoir can be excluded because the CO_2 was injected fully dissolved at a P_{CO2} smaller than the hydrostatic head in the storage reservoir. Carbonate dissolution can also be excluded based on the negative ΔDIC data. The most plausible process for the measured loss in DIC is carbonate mineral precipitation. This is supported by the saturation states of dolomite and calcite, two of the major carbonate phases that are commonly observed in weathered peridotites[25,26,33-35]. Stable carbon isotope ($\delta^{13}C_{DIC}$) in combination with DIC data provide further insight into the governing geochemical processes and the CO_2 reactivity[36-39]. The baseline $\delta^{13}C_{DIC}$ prior to injection was -20.1‰ VPDB, and the injected CO_2 saturated water had a $\delta^{13}C_{DIC}$ value of -33.50‰ VPDB, and thus is depleted by more than 10‰ in ^{13}C compared to the baseline value (Fig. 6). Table S2 shows that the $\delta^{13}C_{DIC}$ values of the collected water samples post-injection ranged from – 32.47 to -36.97‰. Comparing these measured values with the calculated ones based on non-reactive solution-mixing, yields negative $\Delta\delta^{13}C_{DIC}$ values (Table S4). The trend to more negative $\delta^{13}C_{DIC}$ values in addition to the decreasing DIC concentration is indicative of carbonate mineral precipitation[40].

The data obtained during this pilot test and the saturation state calculations indicate precipitation of calcium carbonate or calcium-magnesium carbonate minerals. The source of calcium is undetermined and could be carbonate minerals from pre-existing veins as well as Ca-bearing silicates in peridotite (e.g. pyroxenes and plagioclase)[25]. In addition, alkaline and carbon-depleted groundwater in the storage reservoir is enriched in Ca and mixing between the injected CO_2-saturated solution and the alkaline groundwater results in direct CO_2 uptake via carbon mineralization[22]. Major contribution of calcium from Ca-carbonate-filled veins is unlikely due to a lack of carbonate minerals in veins in the target injection interval from 100 to 400 m depth. Thus, the likely source of Ca is from the dissolution of silicate minerals, as indicated by the increasing Si concentration post injection, and from the alkaline groundwater.

Overall, the results of this pilot study indicate rapid CO_2 mineralisation in peridotite. The acidic pH of the carbonated injection water was neutralized by solution-mixing with alkaline groundwater and by dissolution of the host rock. This led to the precipitation of secondary carbonate minerals and to the storage of the injected CO_2. CO_2 mineralisation rates in peridotite are faster than in basalt, which is likely due to its mineralogy, comprising of fast reacting minerals such as olivine, brucite, lizardite and chrysotile. The analysis of OmanDP core from the test site shows a high degree of serpentinization of the peridotite, with lizardite being the dominant serpentine polymorph and minor chrysotile in veins[29]. However, the alteration (hydration) and vein formation decrease with increasing depth, indicating fresher, potentially more reactive peridotite at greater depth[29]. Furthermore, CO_2 injection into peridotite aquifers, hosting alkaline, Ca-OH-rich groundwater, facilitates rapid carbonate precipitation. Using the collected chemical, stable carbon isotope, and tracer data in mass balance calculations provided quantitative information about in-situ reaction rates and the geochemical fate of the injected CO_2.

This study, previous laboratory experiments and geologic evidence from natural analogues confirm rapid carbon mineralisation rates in peridotite[6,24]. However, porosity, permeability, injectivity and the coupled chemo-mechanical processes during mineralisation are almost unexplored[27]. Porosity measurements of discrete peridotite samples from OmanDP cores show decreasing porosity with increasing depth from maximum 16% in the shallow subsurface to 0.2% at depth[41]. Calculated permeability profiles based on resistivity data also decrease as a function of depth from $\sim 10^{-18}$ m^2 in the shallow subsurface (upper 150 m) to $\sim 10^{-21}$ m^2 (>150 – 400 m). However, permeability and injectivity on a borehole to reservoir scale will be affected by the pervasive fracture network that is observed in peridotites. Injection into ultramafic rocks targets this pre-existing fracture network[27]. Scaling up CO_2 mineralisation in peridotite will depend on the accessibility of these fracture network, and most likely will require some kind of permeability enhancement and remobilization of the fracture network to get industrial scale injection rates.

Carbonation of peridotite results in an increase in solid volume, which could have negative or positive feedbacks. Decreasing permeability by clogging up available pore space is a potential negative feedback of carbonate precipitation in ultramafic rocks. However, natural alkaline springs in the peridotite, formed by hydration and carbonation reaction in the subsurface, persist for hundred thousands of years e.g. in Oman, without any indication of clogging up the reactive flow paths[6,25,26]. This could be explained by a positive feedback mechanism, such as “reaction-driven cracking”. The solid volume increase due to carbonation can induce large differential stresses, which can cause fracturing and thus an increase in permeability and reactive surface area, both necessary to facilitate further rapid mineralisation[42-45]. What governs the different feedback mechanisms is unclear and currently an active field of research that requires coupled lab- and field experiments, as well as numerical approaches[46].

Given the limited volume of the injected CO_2 in this pilot test and all the uncertainties regarding injectivity, permeability and the coupled chemo-mechanical processes, further tests with significantly higher CO_2 injection volumes are necessary. Such tests are currently being conducted or are under development in the United Arab Emirates and the Sultanate of Oman.

Methods

Experimental procedure

A single well push-pull test of a similar type described in Matter et al.[8] and Assayag et al.[36] was conducted, whereby a CO_2-saturated fluid was injected into a hydraulically isolated interval at 100-400 depth in well BA1D over a period of several hours using a borehole packer system. Prior to the CO_2 injection, groundwater was pumped out of well BA1D using a submersible pump and stored in a tank on the surface. In addition, groundwater samples were collected and chemically and isotopically analysed to establish a pre-CO_2 injection baseline. Subsequently, the groundwater in the tank was spiked with potassium bromide (KBr), which was used as a conservative (non-reactive) tracer, and sparged with CO_2 at ~9 atm in a closed system on the surface to form the injection solution (IS). Subsequently, the injection solution was injected (‘push’ phase) at a rate of 10 L/min and a pressure of 10-12 atm at surface into the hydraulic isolated interval in well BA1D below 100 m. The total mass of CO_2 and water injected were 44.0 kg and 8220 litres, respectively. The test lasted for an incubation period of 45 days, during which the injected solution (IS) mixed with the groundwater (GW) via ‘solution-mixing’ in the reservoir and reacted (‘chemical reaction’) with the reservoir rocks. After the 45-day incubation period, the injected solution/groundwater mixture was pumped back (‘pull’ phase) from the hydraulically isolated interval in well BA1D using the packer system and a submersible pump and passed through a measurement cell in which pH, electrical conductivity, temperature, Eh and bromide concentrations were measured. The elapsed pumping time and the extracted fluid volume were recorded, and fluid samples collected from the ‘pull-solution’ for chemical and isotopic analysis.

Analytical methods

Mass balance calculations. Following the approach of Assayag et al.[36] and Matter et al.[17], mixing fractions of the injected solution (IS) and the groundwater (GW) were calculated using following equation for bromide:

$$[Br]_i = X \cdot [Br]_{IS} + (1 - X) \cdot [Br]_{GW} \tag{1}$$

The concentrations of the elements of interest (Ca, Mg, Na, Si) and DIC if no fluid-rock reactions and only non-reactive mixing occurred after the injection (C_i, *predicted*) were calculated using the bromide based mixing fractions and following equation:

$$C_{i,predicted} = X_{Br} \cdot C_{i,IS} + (1 - X_{Br}) \cdot C_{i,GW} \tag{2}$$

with C_i being the concentration of the ith component of interest (Ca, Mg, Na, Si or DIC) in the injection solution (IS), the groundwater (GW) and the predicted water after mixing. Differences of concentrations of the elements of interest and DIC (C_i) between the values measured in the collected fluid samples after the injection and the predicted values based on conservative mixing are defined as:

$$\Delta C_i = C_{i,measured} - C_{i,predicted} \tag{3}$$

Following mass balance equations were used to calculate the predicted $\delta^{13}C_{DIC}$ values[32]:

$$\delta^{13}C_{DIC,predicted} \cdot DIC_{predicted} = X_{Br} \cdot DIC_{IS} \cdot \delta^{13}C_{DIC,IS} + (1 - X_{Br}) \cdot DIC_{GW} \cdot \delta^{13}C_{DIC,GW} \tag{4}$$

which results in:

$$\delta^{13}C_{DIC,predicted} = \left[\frac{DIC_{IS} \cdot \delta^{13}C_{DIC,IS} - DIC_{GW} \cdot \delta^{13}C_{DIC,GW}}{DIC_{IS} - DIC_{GW}}\right] + \left[\frac{DIC_{BW} \cdot DIC_{IS}\left(\delta^{13}C_{DIC,GW} - \delta^{13}C_{DIC,IS}\right)}{DIC_{predicted} \cdot \left(DIC_{IS} - DIC_{GW}\right)}\right] \tag{5}$$

Mineral saturation states were calculated using PHREEQC programme[47], the llnl database and the measured chemical composition, pH, temperature, and ionic strength of the collected fluid samples.

Fluid sample analyses

Concentrations of major ions were measured by inductively coupled plasma optical emission spectroscopy (ICP-OES) for cations using a Perkin-Elmer Optima 4300 DV and for anions by ion chromatography using a Dionex ICS2500, both at the National Oceanography Centre Southampton. Precision and accuracy of ICP-OES analyses based on repeated measurements of diluted in-house seawater standards is better than ±4% for all the elements. For the anion analysis, repeated measurements of single anion standards indicate a precision better than ±1% for Br and Cl analyses.

Dissolved inorganic carbon (DIC) analysis was completed using the VINDTA 3C (Marianda, Germany) at the National Oceanography Centre Southampton, using a coulometric titration (coulometer 5001, UIC, USA). All samples were analyzed at 25°C (±0.1°C) with temperature regulation using a water-bath (Julabo F12, Germany). Repeated measurements on the same batch of seawater ($n \geq 3$) were undertaken every day prior to sample analysis, to assess the precision of the method, which was estimated for the whole dataset to be 1%. Certified Reference Materials (from A.G. Dickson, Scripps Institution of Oceanography) were analysed as standards to calibrate the instrument at the beginning and end of each day of analysis. A daily correction factor was applied to all measured values to standardize the results. Precision, calculated based on repeated measurements of the same in-house standard water samples, was 1%.

The carbon isotopic composition of the DIC samples ($\delta^{13}C_{DIC}$) and gas samples ($\delta^{13}C_{CO2(g)}$, $\delta^{18}O_{CO2(g)}$) were measured using a Delta V Advantage isotope ratio mass spectrometer (IRMS) fitted with a Gasbench II peripheral at the Department of Earth Science, University of Oxford, based on methods described by Assayag et al.[44] The samples were calibrated with NBS-18 and NBS-19 calcite standards dissolved with 100% phosphoric-acid at 18°C. For oxygen isotopes, an acid fractionation factor $\alpha_{CO2(acid)\text{-}calcite} = 1.01053$[49] was used to correct for the difference in acid fractionation factor between the calcite standards and the gas samples. The relative $^{13}C/^{12}C$ values are reported in the conventional $\delta^{13}C$ (‰) notation on the Vienna Pee Dee Belemnite (VPDB) scale, by assigning a value of +1.95‰ to NBS-19. The relative $^{18}O/^{16}O$ values are reported in the conventional $\delta^{18}O$ (‰) notation on the VSMOW-SLAP scale such that the $\delta^{18}O$ of SLAP water was −55.5‰. Precision of $\delta^{13}C_{DIC}$, based on repeat measurements of in-house standard NOCZ-DIC was ±0.16‰ (1σ, n=16), with average $\delta^{13}C_{DIC}$ = 2.16‰ within uncertainty of the long-term average of NOCZ-DIC (2.19‰). Precision of $\delta^{13}C_{CO2(g)}$, $\delta^{18}O_{CO2(g)}$ were 0.03‰ and 0.05‰ (1σ, n=4) respectively.

Declaration of competing interest

The authors declare following competing interests: Co-authors Hasan, Tasfai and Khimji are inventors on patent US17/705,792 and EP22175231,4A , 'System and method for permanent carbon dioxide sequestration using a renewable energy source'. Columbia University, Kelemen and Matter hold US Patent 8524152, 'Systems and methods for enhancing rates of in situ carbonation in peridotite'. All other authors have no competing interests to declare.

Acknowledgments

The project received funding from the ClimateWorks Foundation (Fluxx Grant # G-21030802317354, grant no. 21-1839). Boreholes and borehole straddle packer system used for the experiments were funded through the Oman Drilling Project, which was supported by the Alfred P. Sloan Foundation (in association with the Deep Carbon Observatory, DCO), the International Continental Scientific Drilling Program (ICDP), US National Science Foundation (NSF; grants # NSF-EAR-1516300, EAR-1516313), the Japanese Marine Science and Technology Center (JAMSTEC), the Japanese Society for the Promotion of Science (JSPS; grant # 16H06347) and the European Research Council.

Data Availability

All data required to evaluate the conclusions in the paper are available from Open Science Framework (DOI 10.17605/OSF.IO/5KGW).

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Additional information

Supplementary information The online version contains supplementary material

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Figure Captions

Figure 1. Geological maps of the Multi-borehole Observatory (MBO).
The map on the left is a general geological map, showing the main rock formations, structural features (MTZ: Mantle Transition Zone) and borehole locations. The map on the right is a specific map of the inset area, showing elevation contours as dashed gray lines (interval 5 m, from 550 to 590 masl) and the cluster of the BA boreholes.

Figure 2. Bromide concentration in 'pull solution' samples post CO_2 injection.
Bromide tracer concentrations measured in collected fluid samples from well BA1D after the dissolved CO_2 injection and 45 days of incubation period.

Figure 3. Time series of ion concentrations (predicted vs. measured) in 'pull solution' samples post CO_2 injection.
a measured and predicted calcium concentration vs. pumping time. **b** measured and predicted sodium concentration vs. pumping time. **c** measured and predicted DIC (dissolved inorganic carbon) concentration vs. pumping time. **d** measured and predicted magnesium concentration vs. pumping time. **e** measured and predicted silicon concentration vs. pumping time.

Figure 4. Saturation indices (SI) of major minerals.
Calculated **s**aturation indices (SI) of the collected fluid samples with respect to brucite, chalcedony, chrysotile, enstatite and forsterite. Positive, negative and zero SI values correspond to the fluids being supersaturated, undersaturated and at equilibrium with the specific mineral.

Figure 5. Saturation indices of major carbon-bearing minerals.
Calculated saturation indices (SI) of the collected fluid samples with respect to calcite, hydromagnesite, dolomite and magnesite. Positive, negative and zero SI values correspond to the fluids being supersaturated, undersaturated and at equilibrium with the specific mineral.

Figure 6. Stable carbon isotope ratio ($\delta^{13}C_{DIC}$) of dissolved inorganic carbon.
Relationship between $\delta^{13}C_{DIC}$ and DIC concentration in collected fluid samples after the incubation period of 45 days. Calculated values are the predicted concentrations and carbon isotopic composition based on non-reactive mixing (see Eq. 5). The predicted values plot along a mixing hyperbola between the injected solution and the background reservoir fluid.

Table 1. Pre-injection conditions, cation, anion concentrations and stable carbon isotope ratio.

Sample ID	Groundwater	Injection Solution
T (ºC)	35.20	35.00
pH	11.02	4.10
conductivity (mS/cm)	1.70	1.70
Ca (mmol/L)	3.61	1.73
Mg (mmol/L)	0.002	0.55
Na (mmol/L)	5.49	2.23
Si (mmol/L)	0.012	0.004
Br (mmol/L)	0.00	4.42
Br (ppm)	0.00	353.20
Cl (mmol/L)	8.70	4.32
SO_4^{2-} (mmol/L)	0.57	0.60
DIC (mmol/L)	154.80	122,300.00
$\delta^{13}C_{DIC}$ (‰VPDB)	-20.10	-33.50

Table S2. Ion concentrations and stable carbon isotope ratios of 'pull-solution' samples post-injection

Sample #	Sampling Date & Time	pH	Ca (mmol/L)	Mg (mmol/L)	Na (mmol/L)	Si (mmol/L)	Br (mmol/L)	Br (ppm)	Cl (mmol/L)	SO_4^{2-} (mmol/L)	DIC (μmol/L)	$^{13}C/^{12}C_{DIC}$ (‰VPDB)
23	28/02/22 10:00:00	7.45	1.09	2.62	2.91	0.58270	0.72	57.20	4.42	0.43	6366.24	
30	28/02/22 10:30:00	7.40	1.02	2.36	3.13	0.57110	0.68	54.14	4.55	0.40	5694.69	
32	28/02/22 11:00:00	7.41	0.92	1.92	3.24	0.56302	0.63	50.65	4.56	0.36	4766.85	
36	28/02/22 12:00:00	8.04	0.65	0.58	3.53	0.57771	0.49	38.76	4.45	0.24	1936.08	-35.18
43	28/02/22 14:00:00	8.11	0.55	0.37	3.92	0.56885	0.39	31.41	4.78	0.22	1386.54	-34.92
50	28/02/22 14:30:00	8.16	0.56	0.34	4.07	0.57630	0.37	29.67	4.94	0.25	1304.28	
52	28/02/22 15:00:00	8.16	0.56	0.34	4.12	0.56495	0.37	29.27	5.04	0.25	1280.30	
54	28/02/22 15:30:00	8.20	0.57	0.33	4.15	0.56391	0.34	27.14	4.93	0.24	1223.84	
56	28/02/22 16:00:00	8.22	0.60	0.31	4.27	0.56910	0.34	27.47	5.18	0.24	1170.71	-35.78
63	28/02/22 18:00:00	7.87	0.71	0.45	4.39	0.58664	0.32	25.53	5.58	0.25	1405.53	-36.16
70	28/02/22 18:30:00	7.75	0.69	0.46	4.41	0.59658	0.32	25.36	5.71	0.26	1399.74	
72	28/02/22 19:15:00	7.77	0.72	0.48	4.46	0.60395	0.31	24.52	5.67	0.25	1419.38	
74	01/03/22 10:00:00	7.85	1.06	0.47	4.43	0.60298	0.30	23.62	5.75	0.25	1411.00	-35.33
81	01/03/22 10:30:00	7.73	0.75	0.50	4.45	0.60999	0.31	24.48	5.66	0.25	1524.95	
83	01/03/22 11:00:00	7.69	0.75	0.48	4.44	0.57730	0.31	24.41	5.67	0.26	1524.49	
85	01/03/22 11:30:00	7.74	0.73	0.49	4.39	0.58442	0.30	24.37	5.62	0.24	1519.03	
87	01/03/22 12:00:00	7.86	0.73	0.45	4.41	0.58210	0.31	25.15	5.63	0.24	1453.04	-35.97
94	01/03/22 12:30:00	7.95	0.74	0.45	5.03	0.58658	0.30	24.09	6.46	0.27	1285.91	
96	01/03/22 14:30:00	8.06	0.73	0.28	4.49	0.61849	0.28	22.69	5.71	0.24	1049.41	-35.78
103	01/03/22 15:00:00	8.02	0.74	0.34	4.42	0.61582	0.28	22.47	5.74	0.24	1174.75	
105	01/03/22 15:30:00	7.94	0.76	0.38	4.48	0.61726	0.28	22.39	5.82	0.25	1239.55	

Table S2 (continued) Ion concentrations and stable carbon isotope ratios of ‘pull-solution’ samples post-injection

Sample #	Sampling Date & Time	pH	Ca (mmol/L)	Mg (mmol/L)	Na (mmol/L)	Si (mmol/L)	Br (mmol/L)	Br (ppm)	Cl (mmol/L)	SO_4^{2-} (mmol/L)	DIC (μmol/L)	$^{13}C/^{12}C_{DIC}$ (‰VPDB)
107	01/03/22 16:00:00	7.80	0.76	0.39	4.44	0.61580	0.28	22.43	5.83	0.24	1249.97	
109	01/03/22 16:30:00	7.77	0.80	0.40	4.52	0.62851	0.28	22.12	5.86	0.24	1231.50	
111	01/03/22 17:00:00	7.83	0.80	0.38	4.53	0.62638	0.28	22.13	5.96	0.25	1203.66	-34.71
118	01/03/22 17:30:00	7.75	0.82	0.39	4.53	0.63597	0.27	21.57	5.91	0.25	1202.23	
120	01/03/22 18:00:00	7.86	0.83	0.38	4.52	0.63391	0.26	20.63	5.97	0.25	1178.89	
122	01/03/22 18:30:00	7.84	0.84	0.37	4.51	0.63491	0.26	20.89	6.02	0.25	1179.75	
124	02/03/22 09:30:00	7.69	0.88	0.36	4.64	0.64402	0.25	20.12	6.11	0.25	1164.72	-34.17
131	02/03/22 10:00:00	7.71	0.87	0.38	4.54	0.62205	0.27	21.33	5.97	0.25	1256.42	
135	02/03/22 11:00:00	7.88	0.86	0.37	4.55	0.61833	0.26	20.90	5.94	0.23	1241.03	
139	02/03/22 12:00:00	7.95	0.86	0.35	4.55	0.62970	0.24	19.51	5.92	0.24	1175.91	-35.87
146	02/03/22 14:30:00	8.02	0.85	0.24	4.54	0.63262	0.25	19.94	5.99	0.24	877.20	-34.48
153	02/03/22 15:00:00	7.99	0.86	0.25	4.55	0.63176	0.24	18.94	5.99	0.24	914.19	
157	02/03/22 16:00:00	7.86	0.89	0.31	4.59	0.64725	0.25	19.70	6.07	0.24	1032.08	
161	02/03/22 17:00:00	8.04	0.89	0.33	4.57	0.63411	0.24	19.36	6.09	0.24	1063.99	-35.15
167	02/03/22 17:30:00	7.86	0.90	0.33	4.59	0.63650	0.25	19.93	6.10	0.25	1063.09	
171	03/03/22 09:30:00	7.95	1.32	0.29	4.72	0.65936	0.20	15.95	6.94	0.31	872.62	-34.91
178	03/03/22 10:30:00	8.03	1.35	0.31	4.73	0.66476	0.19	15.16	6.97	0.30	907.37	
182	03/03/22 12:30:00	8.18	1.38	0.29	4.76	0.66303	0.19	15.31	7.08	0.31	844.32	-35.35
189	03/03/22 16:30:00	8.07	1.42	0.31	4.77	0.66065	0.19	15.17	7.18	0.29	892.72	-34.89
196	03/03/22 17:30:00	8.01	1.47	0.29	4.73	0.66344	0.19	15.50	7.10	0.29	858.83	
200	04/03/22 09:30:00	8.24	1.55	0.25	4.85	0.66350	0.17	13.69	7.28	0.34	739.77	-34.46

Table S2 (continued) Ion concentrations and stable carbon isotope ratios of 'pull-solution' samples post-injection

Sample #	Sampling Date & Time	pH	Ca (mmol/L)	Mg (mmol/L)	Na (mmol/L)	Si (mmol/L)	Br (mmol/L)	Br (ppm)	Cl (mmol/L)	SO_4^{2-} (mmol/L)	DIC (μmol/L)	$^{13}C/^{12}C_{DIC}$ (‰VPDB)
209	04/03/22 11:30:00	8.30	1.56	0.24	4.83	0.64957	0.17	13.49	7.24	0.33	727.05	
211	04/03/22 12:30:00	8.28	1.57	0.26	4.86	0.65141	0.19	14.85	7.38	0.37	754.12	-36.35
218	04/03/22 20:00:00	8.40	1.65	0.25	4.85	0.63353	0.18	14.02	7.54	0.39	734.55	-36.95
225	05/03/22 10:00:00	8.48	1.60	0.19	4.82	0.62493	0.17	13.79	7.33	0.36	612.78	-36.26
241	05/03/22 16:30:00	8.51	1.71	0.23	4.95	0.61952	0.17	13.42	7.60	0.41	646.85	
245	05/03/22 18:00:00	8.56	1.74	0.24	4.96	0.61567	0.16	13.16	7.58	0.39	652.57	-36.97
252	06/03/22 10:00:00	8.71	1.80	0.22	4.91	0.58113	0.15	12.28	7.71	0.44	518.19	-35.95
259	06/03/22 11:00:00	8.71	1.80	0.21	4.93	0.58179	0.15	12.18	7.74	0.45	519.52	
263	06/03/22 13:00:00	8.73	1.90	0.20	4.98	0.58176	0.15	12.05	7.74	0.42	626.56	-36.30
272	06/03/22 18:30:00	8.80	1.89	0.20	4.87	0.56380	0.15	11.66	7.71	0.43	560.30	-36.53
279	07/03/22 09:30:00	8.82	1.92	0.16	4.92	0.54843	0.14	11.32	7.76	0.47	458.21	
286	07/03/22 10:30:00	8.80	1.92	0.16	4.91	0.54916	0.14	11.26	7.84	0.45	432.67	
290	07/03/22 12:30:00	8.82	1.91	0.15	4.93	0.55310	0.14	11.25	7.73	0.44	413.61	-35.16
299	07/03/22 18:30:00	8.86	1.91	0.18	5.05	0.53728	0.14	11.02	7.97	0.47	434.54	-34.85
306	08/03/22 10:00:00	8.90	1.93	0.15	4.97	0.52187	0.14	10.83	7.80	0.51	340.46	-32.47
313	08/03/22 11:00:00	8.91	1.88	0.14	4.82	0.50683	0.13	10.74	7.87	0.48	326.86	
317	08/03/22 17:00:00	9.00	1.93	0.15	4.94	0.50707	0.13	10.38	7.82	0.48	318.79	-35.67
326	09/03/22 09:30:00	9.07	1.95	0.12	5.01	0.48711	0.13	10.14	7.84	0.49	201.90	-33.64
335	09/03/22 11:30:00	9.12	1.92	0.12	4.87	0.47451	0.13	10.06	7.86	0.51	212.49	-34.95

Table S2 (continued) Ion concentrations and stable carbon isotope ratios of ‘pull-solution’ samples post-injection

Sample #	Sampling Date & Time	pH	Ca (mmol/L)	Mg (mmol/L)	Na (mmol/L)	Si (mmol/L)	Br (mmol/L)	Br (ppm)	Cl (mmol/L)	SO_4^{2-} (mmol/L)	DIC (μmol/L)	$^{13}C/^{12}C_{DIC}$ (‰VPDB)
344	09/03/22 18:00:00	9.19	1.91	0.12	4.88	0.46892	0.12	9.88	7.80	0.53	168.66	-32.87
351	10/03/22 09:30:00	9.24	1.93	0.10	4.96	0.45388	0.12	9.54	7.91	0.54	117.58	-35.90
360	10/03/22 11:30:00	9.31	1.96	0.10	5.04	0.45949	0.12	9.73	7.86	0.57	113.09	-36.13
369	10/03/22 18:00:00	9.40	1.95	0.08	4.98	0.44503	0.12	9.73	8.02	0.60	101.60	-36.46
376	11/03/22 09:30:00	9.50	2.01	0.08	4.99	0.43092	0.11	9.01	7.81	0.52	83.26	-34.49
383	11/03/22 10:30:00	9.50	1.95	0.08	5.02	0.43317	0.12	9.30	7.85	0.54	84.33	-36.24

Table S3. Mixing fractions and calculated concentrations assuming non-reactive solution mixing

Sample #	Cumulative pumped volume (L)	Dilution factor	Fraction of injected solution[a]	Fraction of background water[a]	predicted concentrations[b]					
					Ca (mmol/L)	Mg (mmol/L)	Na (mmol/L)	Si (mmol/L)	DIC (μmol/L)	$\delta^{13}C_{DIC}$ (‰VPDB)
23	179.60	6.17	0.16	0.84	3.31	0.087	4.96	0.011	19945.44	-33.41
30	357.08	6.52	0.15	0.85	3.32	0.083	4.99	0.011	18889.73	-33.41
32	643.10	6.97	0.14	0.86	3.34	0.077	5.02	0.011	17681.08	-33.40
36	1133.69	9.11	0.11	0.89	3.41	0.060	5.13	0.011	13564.82	-33.36
43	2082.13	11.24	0.09	0.91	3.44	0.049	5.20	0.012	11023.30	-33.33
50	2306.16	11.90	0.08	0.92	3.45	0.046	5.22	0.012	10422.61	-33.32
52	2539.18	12.06	0.08	0.92	3.46	0.046	5.22	0.012	10282.47	-33.32
54	2758.20	13.01	0.08	0.92	3.47	0.042	5.24	0.012	9544.06	-33.30
56	2828.44	12.85	0.08	0.92	3.47	0.043	5.24	0.012	9660.67	-33.30
63	3767.19	13.82	0.07	0.93	3.48	0.040	5.26	0.012	8990.08	-33.29
70	3996.97	13.92	0.07	0.93	3.48	0.040	5.26	0.012	8930.22	-33.29
72	4321.21	14.40	0.07	0.93	3.48	0.039	5.26	0.012	8638.53	-33.28
74	4345.84	14.95	0.07	0.93	3.49	0.037	5.27	0.012	8326.76	-33.27
81	4345.84	14.42	0.07	0.93	3.48	0.039	5.26	0.012	8626.76	-33.28
83	4687.16	14.46	0.07	0.93	3.48	0.038	5.27	0.012	8601.50	-33.28
85	4883.31	14.49	0.07	0.93	3.48	0.038	5.27	0.012	8587.32	-33.28
87	5039.63	14.04	0.07	0.93	3.48	0.040	5.26	0.012	8856.17	-33.28
94	5148.52	14.65	0.07	0.93	3.48	0.038	5.27	0.012	8490.78	-33.27
96	6025.53	15.56	0.06	0.94	3.49	0.036	5.28	0.012	8004.62	-33.26
103	6154.90	15.71	0.06	0.94	3.49	0.036	5.28	0.012	7929.53	-33.26
105	6288.81	15.76	0.06	0.94	3.49	0.035	5.28	0.012	7902.89	-33.26

Table S3 (continued). Mixing fractions and calculated concentrations assuming non-reactive solution mixing

Sample #	Cumulative pumped volume (L)	Dilution factor	Fraction of injected solution[a]	Fraction of background water[a]	predicted concentrations[b]					
					Ca (mmol/L)	Mg (mmol/L)	Na (mmol/L)	Si (mmol/L)	DIC (μmol/L)	$\delta^{13}C_{DIC}$ (‰VPDB)
107	6472.40	15.74	0.06	0.94	3.49	0.035	5.28	0.012	7915.35	-33.26
109	6566.24	15.96	0.06	0.94	3.49	0.035	5.29	0.012	7809.81	-33.25
111	6800.42	15.95	0.06	0.94	3.49	0.035	5.29	0.012	7812.23	-33.25
118	6927.69	16.37	0.06	0.94	3.50	0.034	5.29	0.012	7617.08	-33.25
120	4687.16	17.11	0.06	0.94	3.50	0.033	5.30	0.012	7293.20	-33.23
122	7294.40	16.90	0.06	0.94	3.50	0.033	5.30	0.012	7383.51	-33.24
124	7426.57	17.54	0.06	0.94	3.50	0.032	5.31	0.012	7116.73	-33.23
131	7620.28	16.55	0.06	0.94	3.50	0.034	5.29	0.012	7536.80	-33.24
135	7938.89	16.89	0.06	0.94	3.50	0.033	5.30	0.012	7385.93	-33.24
139	8175.18	18.09	0.06	0.94	3.51	0.031	5.31	0.012	6906.00	-33.22
146	8820.40	17.70	0.06	0.94	3.51	0.032	5.31	0.012	7054.79	-33.22
153	8948.67	18.64	0.05	0.95	3.51	0.030	5.32	0.012	6708.08	-33.21
157	9166.87	17.92	0.06	0.94	3.51	0.031	5.31	0.012	6970.02	-33.22
161	9385.47	18.23	0.05	0.95	3.51	0.031	5.31	0.012	6855.14	-33.22
167	4321.21	17.71	0.06	0.94	3.51	0.032	5.31	0.012	7051.33	-33.22
171	14887.67	22.13	0.05	0.95	3.53	0.026	5.34	0.012	5673.83	-33.15
178	15266.68	23.28	0.04	0.96	3.53	0.025	5.35	0.012	5401.51	-33.14
182	15693.60	23.05	0.04	0.96	3.53	0.025	5.35	0.012	5453.41	-33.14
189	17073.66	23.27	0.04	0.96	3.53	0.025	5.35	0.012	5404.28	-33.14
196	17368.27	22.78	0.04	0.96	3.53	0.025	5.35	0.012	5517.42	-33.14
200	22140.42	25.79	0.04	0.96	3.54	0.022	5.36	0.012	4890.09	-33.10

Table S3 (continued). Mixing fractions and calculated concentrations assuming non-reactive solution mixing

Sample #	Cumulative pumped volume (L)	Dilution factor	Fraction of injected solution[a]	Fraction of background water[a]	predicted concentrations[b]					
					Ca (mmol/L)	Mg (mmol/L)	Na (mmol/L)	Si (mmol/L)	DIC (µmol/L)	$\delta^{13}C_{DIC}$ (‰VPDB)
209	22935.67	26.16	0.04	0.96	3.54	0.022	5.37	0.012	4824.00	-33.09
211	23314.84	23.78	0.04	0.96	3.53	0.024	5.35	0.012	5291.47	-33.13
218	26062.32	25.19	0.04	0.96	3.54	0.023	5.36	0.012	5004.28	-33.10
225	28924.85	25.60	0.04	0.96	3.54	0.023	5.36	0.012	4926.08	-33.10
241	31687.64	26.30	0.04	0.96	3.54	0.022	5.37	0.012	4798.74	-33.09
245	32302.47	26.83	0.04	0.96	3.54	0.022	5.37	0.012	4706.70	-33.08
252	38720.78	28.74	0.03	0.97	3.55	0.020	5.38	0.012	4404.62	-33.05
259	39171.95	28.99	0.03	0.97	3.55	0.020	5.38	0.012	4367.94	-33.04
263	40125.76	29.29	0.03	0.97	3.55	0.020	5.38	0.012	4324.69	-33.04
272	42590.03	30.28	0.03	0.97	3.55	0.019	5.38	0.012	4188.01	-33.02
279	48910.42	31.19	0.03	0.97	3.55	0.019	5.39	0.012	4071.40	-33.01
286	49287.37	31.34	0.03	0.97	3.55	0.019	5.39	0.012	4052.37	-33.01
290	50083.73	31.38	0.03	0.97	3.55	0.019	5.39	0.012	4047.53	-33.01
299	52610.48	32.03	0.03	0.97	3.55	0.019	5.39	0.012	3968.64	-33.00
306	58576.01	32.59	0.03	0.97	3.55	0.018	5.39	0.012	3902.55	-32.99
313	58930.30	32.86	0.03	0.97	3.55	0.018	5.39	0.012	3872.44	-32.98
317	12488.11	33.99	0.03	0.97	3.56	0.018	5.40	0.012	3747.88	-32.97
326	69240.82	34.80	0.03	0.97	3.56	0.017	5.40	0.012	3664.83	-32.95
335	69969.10	35.09	0.03	0.97	3.56	0.017	5.40	0.012	3636.11	-32.95

Table S3 (continued). Mixing fractions and calculated concentrations assuming non-reactive solution mixing

Sample #	Cumulative pumped volume (L)	Dilution factor	Fraction of injected solution[a]	Fraction of background water[a]	predicted concentrations[b]					
					Ca (mmol/L)	Mg (mmol/L)	Na (mmol/L)	Si (mmol/L)	DIC (μmol/L)	$\delta^{13}C_{DIC}$ (‰VPDB)
344	72861.42	35.72	0.03	0.97	3.56	0.017	5.40	0.012	3574.17	-32.94
351	75233.69	37.01	0.03	0.97	3.56	0.016	5.40	0.012	3454.80	-32.92
360	81003.13	36.28	0.03	0.97	3.56	0.017	5.40	0.012	3521.23	-32.93
369	83981.78	36.29	0.03	0.97	3.56	0.017	5.40	0.012	3520.89	-32.93
376	90657.52	39.19	0.03	0.97	3.56	0.016	5.41	0.012	3271.75	-32.89
383	90657.52	37.96	0.03	0.97	3.56	0.016	5.41	0.012	3372.44	-32.91

[a] Calculated using Eq. 1 and data from Table 1 and 2.

[b] Calculated using Eq.2 or Eqs. 4 and 5, and data from Table 1 and 2.

Supplementary Information

Table S4. Chemical and isotopic mass balances of 'pull-solution' samples, calculated using Eq.3

Sample #	ΔCa mmol/L	ΔMg mmol/L	ΔNa mmol/L	ΔSi mmol/L	$\Delta\delta^{13}C_{DIC}$ (‰VPDB)
23	-2.22	2.53	-2.05	0.57	
30	-2.30	2.28	-1.87	0.56	
32	-2.43	1.84	-1.79	0.55	
36	-2.76	0.52	-1.60	0.57	-1.81
43	-2.89	0.32	-1.29	0.56	-1.59
50	-2.89	0.30	-1.15	0.56	
52	-2.90	0.30	-1.10	0.55	
54	-2.90	0.29	-1.09	0.55	
56	-2.87	0.27	-0.97	0.56	-2.48
63	-2.77	0.41	-0.86	0.57	-2.87
70	-2.79	0.42	-0.85	0.58	
72	-2.76	0.44	-0.80	0.59	
74	-2.43	0.43	-0.85	0.59	-2.06
81	-2.73	0.46	-0.82	0.60	
83	-2.73	0.45	-0.83	0.57	
85	-2.75	0.45	-0.88	0.57	
87	-2.75	0.41	-0.84	0.57	-2.69
94	-2.75	0.41	-0.24	0.57	
96	-2.76	0.25	-0.79	0.61	-2.52
103	-2.75	0.31	-0.86	0.60	
105	-2.73	0.35	-0.81	0.61	
107	-2.73	0.35	-0.85	0.60	
109	-2.69	0.36	-0.77	0.62	
111	-2.70	0.35	-0.76	0.61	-1.45
118	-2.68	0.35	-0.76	0.62	
120	-2.67	0.35	-0.78	0.62	
122	-2.66	0.34	-0.79	0.62	
124	-2.62	0.33	-0.66	0.63	-0.95
131	-2.63	0.35	-0.75	0.61	
135	-2.64	0.33	-0.75	0.61	
139	-2.65	0.32	-0.76	0.62	-2.65
146	-2.66	0.21	-0.77	0.62	-1.25
153	-2.65	0.22	-0.76	0.62	
157	-2.62	0.28	-0.72	0.64	
161	-2.62	0.30	-0.74	0.62	-1.93
167	-2.61	0.30	-0.71	0.62	
171	-2.21	0.27	-0.62	0.65	-1.75
178	-2.18	0.28	-0.62	0.65	

Table S4 (continued). Chemical and isotopic mass balances of 'pull-solution' samples, calculated using Eq.3

Sample #	ΔCa mmol/L	ΔMg mmol/L	ΔNa mmol/L	ΔSi mmol/L	$\Delta\delta^{13}C_{DIC}$ (‰VPDB)
182	-2.15	0.26	-0.59	0.65	-2.22
189	-2.11	0.29	-0.58	0.65	-1.75
196	-2.06	0.27	-0.62	0.65	
200	-1.99	0.22	-0.51	0.65	-1.36
209	-1.98	0.22	-0.54	0.64	
211	-1.96	0.24	-0.49	0.64	-3.22
218	-1.89	0.23	-0.51	0.62	-3.84
225	-1.94	0.17	-0.55	0.61	-3.16
241	-1.83	0.21	-0.42	0.61	
245	-1.80	0.22	-0.41	0.60	-3.89
252	-1.75	0.19	-0.47	0.57	-2.91
259	-1.75	0.19	-0.45	0.57	
263	-1.65	0.18	-0.40	0.57	-3.26
272	-1.66	0.18	-0.51	0.55	-3.50
279	-1.63	0.14	-0.46	0.54	
286	-1.63	0.14	-0.48	0.54	
290	-1.64	0.13	-0.46	0.54	-2.15
299	-1.64	0.17	-0.33	0.53	-1.86
306	-1.62	0.13	-0.42	0.51	0.51
313	-1.68	0.12	-0.57	0.49	
317	-1.63	0.13	-0.46	0.49	-2.70
326	-1.61	0.10	-0.39	0.48	-0.68
335	-1.63	0.11	-0.53	0.46	-2.00
344	-1.65	0.10	-0.52	0.46	0.07
351	-1.63	0.08	-0.44	0.44	-2.98
360	-1.60	0.08	-0.36	0.45	-3.20
369	-1.61	0.07	-0.42	0.43	-3.53
376	-1.55	0.06	-0.42	0.42	-1.60
383	-1.61	0.06	-0.38	0.42	-3.34