

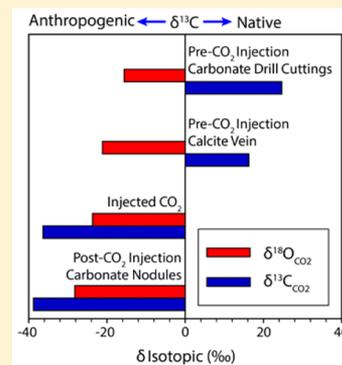
Field Validation of Supercritical CO₂ Reactivity with Basalts

B. Peter McGrail,^{*,†} Herbert T. Schaef,[‡] Frank A. Spane, John B. Cliff, Odeta Qafoku, Jake A. Horner, Christopher J. Thompson, Antoinette T. Owen, and Charlotte E. Sullivan

Pacific Northwest National Laboratory, P.O. Box 999, Richland, Washington 99352, United States

Supporting Information

ABSTRACT: Continued global use of fossil fuels places a premium on developing technology solutions to minimize increases in atmospheric CO₂ levels. CO₂ storage in reactive basalts might be one of these solutions by permanently converting gaseous CO₂ into solid carbonates. Herein, we report results from a field demonstration in which ~1000 metric tons of CO₂ was injected into a natural basalt formation in eastern Washington state. Following post-injection monitoring for 2 years, cores were obtained from within the injection zone and subjected to detailed physical and chemical analysis. Nodules found in vesicles throughout the cores were identified as the carbonate mineral, ankerite Ca[Fe,Mg,Mn](CO₃)₂. Carbon isotope analysis showed the nodules are chemically distinct compared with natural carbonates present in the basalt and in clear correlation with the isotopic signature of the injected CO₂. These findings provide field validation of rapid mineralization rates observed from years of laboratory testing with basalts.



INTRODUCTION

In November 2015, leaders from 195 nations gathered in Paris at the United Nations Climate Change Conference, COP21, to forge an international agreement on emission cuts and other actions through 2030.¹ Achieving these goals is a very complex problem, and a mix of solutions is required, including innovative technologies, enhanced conservation measures, and modifications to social behaviors that can lead to a global energy transformation.

The concept of carbon capture and sequestration (CCS) is one emerging technology in a suite of mitigation strategies. The idea involves capturing CO₂ from anthropogenic point sources and injecting it into subsurface geologic formations for permanent storage.² It is a method that allows continued accrual of societal benefits from the use of cheap and abundant fossil fuels while helping to lower the maximal CO₂ concentration our planet will experience over the balance of this century.³ If CCS becomes a key part of a comprehensive energy policy, the availability of regional and local deployment options is needed. Expanding options for CCS has been the principal motivation behind years of scientific research investigating the potential of continental basalt provinces to serve as storage reservoirs for anthropogenic CO₂.^{4–6} The ability of basalts to rapidly convert CO₂ into a solid carbonate mineral has been proven in the laboratory.^{7,8} Mineralization of CO₂ inherently attractive because once converted to carbonates, the CO₂ cannot escape to potentially impact shallow aquifers or return to the atmosphere. However, there is ample evidence in the geochemical literature to temper enthusiasm about laboratory observations of rapid geochemical reactions as these often prove to be orders of magnitude faster than reactions that actually occur in the field.^{9–11} Field testing is

realistically the only way to ascertain how relevant laboratory mineralization rates are to in situ conditions.

Currently, there are two field tests ongoing evaluating injection of CO₂ into basalts.^{12,13} The CarbFix project in Iceland injected CO₂ predissolved in water, whereas the Wallula Basalt Pilot Project located in eastern Washington state was always planned around injection with conventional pressurized liquid CO₂. There are pros and cons for each approach that have been previously discussed.^{12,14} The most recent findings from the CarbFix project suggest 95% of the injected CO₂ was converted to carbonate minerals in <2 years.¹⁵ We report here on findings after post-injection monitoring for 2 years on the Wallula Basalt Pilot Project.

MATERIALS AND METHODS

X-ray Diffraction (XRD), Scanning Electron Microscopy with Energy-Dispersive X-ray Spectroscopy (SEM–EDS), and X-ray Microtomography (XMT). Whole sidewall cores, collected pre-CO₂ (856.7 m) and post-CO₂ injection (856.5 and 857.1 m) within the Grand Ronde Formation, were imaged with a real time XMT system (Northstar Imaging Inc.). Carbonate nodules removed from the sidewall cores were crushed, mounted into a glass capillary tube, and characterized on a D8 Discover X-ray diffractometer. Cross sectional chemical profiles of polished epoxy-mounted carbonate nodule sections were obtained from a dual-beam scanning electron microscope equipped with an EDX detector that was used for qualitative analysis. More experimental details on each

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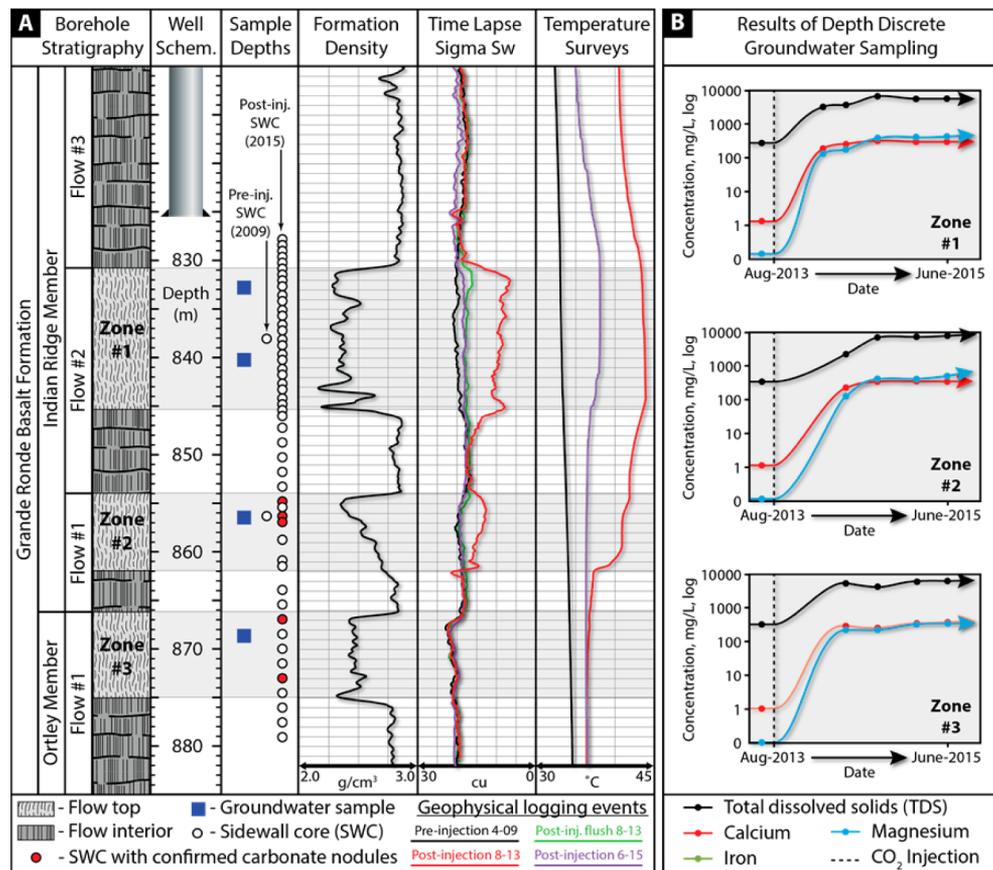


Figure 1. Detailed characteristics of well bore properties over the duration of the project. (A) Basalt stratigraphy, well bore schematic, water sampling depths, sidewall core locations, formation density survey (grams per cubic centimeter), time-lapse water saturation survey before and after CO₂ injection (cu), and borehole temperature profile survey (degrees Celsius). (B) Groundwater chemistry obtained from preinjected formation water, postinjected water (four separate samplings), and water used to flush the borehole after injection.

characterization technique are provided in the [Supporting Information](#).

Nano Secondary Ion Mass Spectrometry (NanoSIMS).

The NanoSIMS analyses were performed over three separate analytical sessions with two sessions devoted to oxygen isotopes and one session devoted to carbon isotopes. The sample was presputtered with an ~ 2 nA, 16 keV Cs⁺ primary beam using a 25 $\mu\text{m} \times 25 \mu\text{m}$ raster followed by automatic centering of the secondary beam in horizontal and vertical axes and automatic centering of EOS. An electron gun was used for charge compensation. Secondary ions (¹⁶O⁻ and ¹⁸O⁻, or ¹²C⁻ and ¹³C⁻) were collected in dual Faraday cup detectors with a 20 $\mu\text{m} \times 20 \mu\text{m}$ raster for 40 \times 5 s integrations. Three to eight unknowns were bracketed by seven or eight standard analyses. The internal precision averaged 0.3‰ (1 σ) for oxygen isotopes and 0.7‰ for carbon isotopes. The external precision for the standard analyses was 0.14 and 0.3‰ for the oxygen sessions and 0.6‰ for carbon isotopes. $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ are reported against VPDB. More experimental details on the sample preparation are provided in the [Supporting Information](#).

RESULTS AND DISCUSSION

A CO₂ injection well was drilled in 2009 into the Columbia River Basalt (CRB) at the Wallula pilot site to a total depth of 1253 m. Extensive hydrologic characterization during the drilling activity identified a 59 m interval as the candidate injection zone between 828 and 887 m bgs. The injection zone

contains three flowtop/interflow zones (zone 1, zone 2, and zone 3) separated by dense impermeable flow interiors.¹² The upper two interflows lie within the Indian Ridge member, and a bottom interflow section is part of the Ortley member, all situated underneath the massive Umtanum member of the Grande Ronde basalt. The geophysical density survey, which is a diagnostic logging tool for distinguishing porous, low-density basalt flow tops from low-permeability, higher-density basalt flow interior sections, identified distinct density boundaries (Figure 1) that often exceeded 0.5 g/cm³. Transmissivity values in these permeable interflows ranged between 0.69 and 1.8 m²/day, with $\sim 90\%$ coming from the upper injection zone, zone 1.¹² As a benchmark, formation water saturation data were collected and used as a baseline for post-CO₂ injection measurements. The preinjection formation temperature and pressure were ~ 36 °C and ~ 77 bar, respectively.

A series of reservoir tests was conducted in the open borehole section, including hydrologic pump tests and groundwater sampling that confirmed the integrity of the overlying basalt flow interior sections to prevent vertical migration of buoyant CO₂ out of the injection zone. On the basis of these findings, a permit was issued by the State of Washington allowing injection of up to 1000 metric tons (MT) of CO₂. Injection occurred during a 3 week period that concluded in August 2013. Daily injection rates were limited to 40 MT/day to maintain injection pressures within 30% of hydrostatic reservoir conditions.¹² Because CO₂ was stored locally in chilled tanks, the CO₂ was preheated to 44 °C before

being pumped into the well to prevent thermal shock in the well bore and injection zone. This did, however, introduce a small but easily detectable thermal anomaly. A downhole temperature survey collected 20 hour post-injection shows a strong deflection above *in situ* conditions in zone 1, a smaller deviation in zone 2, and essentially no change in zone 3 (Figure 1). The temperature depth profile is thus diagnostic of where the warm CO₂ was flowing with the largest temperature increase correlating to greater penetration of CO₂ into zone 1, consistent with the higher permeability measured for this zone. The persistence of this thermal profile was confirmed in two additional post-CO₂ injection temperature surveys (9 and 22 months). Further evidence of CO₂ disposition was acquired through a series of time-lapse borehole logging surveys measuring changes in fluid and formation characteristics. The neutron capture cross section survey tool revealed significant deviations related to injection zone fluid composition. The baseline survey conducted in 2009 was consistent with a formation saturated with water (Figure 1), whereas the post-CO₂ injection survey indicated CO₂ replaced pore water in zone 1 (75–90%) and zone 2 (40%); no detectable changes to pore fluid were observed in zone 3.

A time-lapse series of discrete groundwater samples obtained from specific depths following the injection of CO₂ were compared to those initially collected in 2009 (Figure 1). As expected, significant changes to the groundwater chemistry occurred following CO₂ injection. On average, the total dissolved solids measured for the pre-CO₂ injection fluid ranged between 149 and 170 mg/L. However, following injection, measured readings exceeded 40 times the original value; alkalinity values trended similarly. Major cation concentrations (Ca, Fe, Mg, K, and Na) were several orders of magnitude above pre-CO₂ injection concentrations. Geochemical calculations⁷ using the fluid chemistry, formation pressure, and temperature show carbonate minerals such as calcite and dolomite as being supersaturated under reservoir conditions.

Closure of the Wallula pilot well was scheduled in the late summer of 2015, and planned activities prior to closure included retrieval of ~50 sidewall cores (SWC) within the injection zone for comparison to SWCs collected preinjection. Visual characterization of SWCs, particularly those positioned within zone 2, identified light-colored opaque globular deposits measuring ~0.1–1 mm in diameter (Figure 2) not previously observed in CRB samples. X-ray microtomographic images showed these nodular deposits existed throughout the SWC within vugs and voids (Figure S1).

Several accessible nodules were extracted from SWC 857.1 m (stratigraphically below the SWC shown in Figure 2) and subjected to structural, chemical, and isotopic analysis. Texturally, the nodules are circumgranular with a complex fabric of sequenced right-angle particles faceted to the surface. Ankerite, Ca[Fe,Mg,Mn](CO₃)₂ (Figure S2), was identified as the sole crystalline component, which is a naturally occurring carbonate mineral that belongs to the dolomite group. Ankerite was previously identified as a secondary reaction product in our laboratory studies where similar CRB samples were reacted with supercritical CO₂ (scCO₂) and water.¹⁶ Additionally, an examination of available drill cuttings and SWCs retrieved in 2009 revealed several broken carbonate mineral fragments in drill cuttings and a brecciated calcite (Figure S2) vein, but no carbonate nodules comparable to those in the post-CO₂ injection SWC sample were identified.

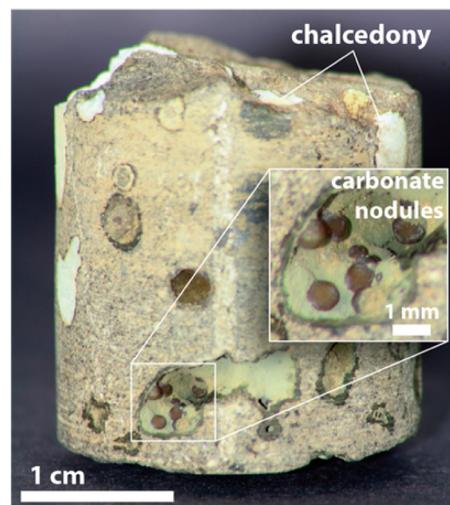


Figure 2. Sidewall core taken from the injection zone (856.5 m) of the Wallula Basalt Pilot Well 24 months after CO₂ injection. Similar nodules from other depths were identified by X-ray diffraction as ankerite, Ca[Fe,Mg,Mn](CO₃)₂, a naturally occurring carbonate mineral.

Chemical profiles obtained from cross sections of three separate nodules extracted from SWC 857.1 m indicate a systematic variation in Ca and Fe, and to a lesser extent Mn. The largest nodule, with a diameter of ~400 μm, was bisected to reveal a second smaller nodule adjoining the top (Figure S3). Chemically, the core of the main nodule is rich in Ca [Ca_{0.62}Fe_{0.24}Mn_{0.14}(CO₃)₂], whereas Fe dominates regions ≥200 μm from the center [Ca_{0.34}Fe_{0.63}Mn_{0.01}(CO₃)₂]. Concentrations of Mn mirror changes observed in Ca content. Although detected only in the outer sections of the nodule rims, Mg concentrations tended to trend opposite that of Mn but never reached concentrations of >0.5 wt %. The adjacent smaller nodule with a cross sectional profile higher up in the particle, evident by the static amounts of Ca and Fe across the profile, closely matched the rim chemistry of the main particle [Ca_{0.34}Fe_{0.63}Mn_{0.01}(CO₃)₂]. The remaining two nodules examined were sectioned off center and therefore did not provide a profile through the core. However, their chemical trends pair well with the nodule in Figure S3. Overall, these ankerite nodules provide a chemical map of sorts that reflects a rapidly evolving pore fluid environment as the basalt reacts with CO₂-charged water. Similar chemically zoned carbonate reaction products were identified in our laboratory studies where CRB is reacted with water and scCO₂.⁷ In contrast, comparable data obtained from the natural calcite vein extracted from SWC 586.1 m indicated pure Ca with no measurable cation substitution.

The distinct differences observed in the crystal structure and elemental composition of the SWC carbonate nodules compared to those of the calcite naturally occurring in the basalts are indicative but not conclusive proof of formation from injected CO₂. Consequently, the nodules were subjected to detailed isotopic composition analysis. δ¹⁸O and δ¹³C ratios were determined for (1) preexisting natural carbonates in the basalt, (2) injected CO₂, and (3) groundwater samples.¹² Isotopic analyses (see Materials and Methods and Table S1) were conducted on three individual nodules and a subsample of the calcite vein obtained from SWC 856.7 m retrieved in 2009 (C and O isotope ratios reported relative to the Vienna Pee

Dee Belemnite standard). On the basis of 21 data points extracted from three individual ankerite nodules, the average $\delta^{18}\text{O}$ value was $22.47 \pm 2.32 \text{‰}$; the average $\delta^{13}\text{C}$ value, based on nine data points, was $-37.72 \pm 2.11 \text{‰}$. The $\delta^{18}\text{O}$ average value for calcite was similar ($-21.1 \pm 0.58 \text{‰}$), but the $\delta^{13}\text{C}$ content ($+15.8 \pm 0.99 \text{‰}$) was disproportionately enriched by comparison. Figure 3 best illustrates differences in $\delta^{18}\text{O}$ and

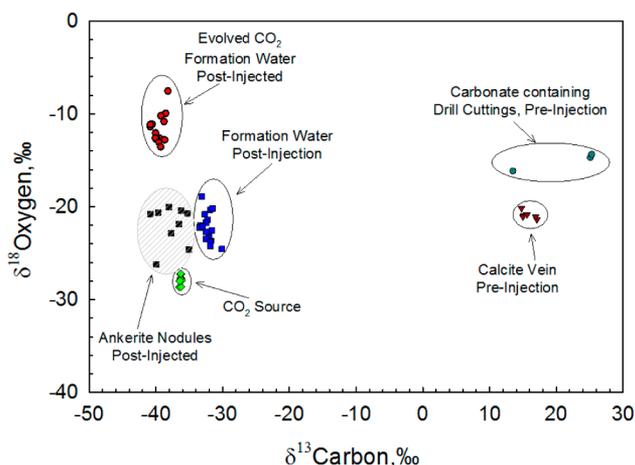


Figure 3. Isotope $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ ratios obtained from samples collected at the Wallula Basalt Pilot Well located in eastern Washington state, which include (1) a pre- CO_2 injection calcite vein from a sidewall core (856.7 m) and (2) postinjection carbonate nodules from SWC (857.1). See Table S1 for analytical methods, the associated laboratory, sample depths, and values used in the graph.

$\delta^{13}\text{C}$ ratios determined for samples obtained post- CO_2 injection and those representing formation under natural conditions (preinjection). Enriched $\delta^{13}\text{C}$ values affiliated with carbonates from pre-injection well bore cuttings are plotted adjacent to natural calcite values and do not cluster with observed $\delta^{13}\text{C}$ groupings from post- CO_2 injection samples. Discrete time-lapse groundwater samples are notably depleted of ^{13}C (-40 and -30‰); outgassed CO_2 from formation waters is more deficient in ^{13}C by comparison, and $\delta^{13}\text{C}$ values for injected CO_2 ($-36.3 \pm 0.09 \text{‰}$) are similar. Most notable is the correlation between $\delta^{13}\text{C}$ values obtained from the ankerite nodules and the injected CO_2 , indicating a common source.¹⁷ Altogether, the evidence is conclusive; the isotopic composition of carbon and oxygen in the ankerite precipitates is distinct from that of the naturally occurring carbonates in the basalt and so could have formed only from the injected CO_2 .

A nominal 1000 MT scCO_2 injection into the Columbia River basalt formation in eastern Washington state was performed. Two years post-injection, core samples extracted from the injection zone showed that carbonate nodules had formed in vugs and veins in the basalt around the injection well. Isotopic analysis of the carbonates conclusively showed the carbonates were derived from the injected CO_2 . Moreover, progressive enrichment of the carbonates in Fe and Mn over time can occur only from dissolution of the primary minerals and glassy mesostasis in the basalt. The progressive enrichment of Fe and Mn in the carbonates formed in the Wallula field test is virtually identical to observations made over several years of laboratory testing with Columbia River and other basalts. As such, these results validate the finding that rapid rates of mineral carbonation are derived from basalt dissolution and not just dissolution and reprecipitation of naturally occurring

calcite. That is perhaps the most important conclusion yet from the Wallula pilot test and supports assumptions we made over a decade ago⁶ about the participation of the entire basalt rock mass in the carbonation reactions, which is necessary to achieve the volume and sustained rates of mineral trapping envisioned for any commercial-scale CO_2 storage project in basalts.

■ ASSOCIATED CONTENT

📄 Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: [10.1021/acs.estlett.6b00387](https://doi.org/10.1021/acs.estlett.6b00387).

Description of XMT, XRD, NanoSIMS, and SEM–EDX techniques, $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values shown in Figure 3, groundwater data supporting Figure 1, three-dimensional image of a SWC, the XRD pattern of carbonate nodules, and a SEM image of carbonate nodules from SWC 857.1 m (PDF)

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: pete.mcgrail@pnnl.gov.

ORCID

Herbert T. Schaeff: [0000-0002-4546-3979](https://orcid.org/0000-0002-4546-3979)

Present Address

†B.P.M.: Pacific Northwest National Laboratory, P.O. Box 999, MS-K4-18, Richland, WA 99352.

Notes

The authors declare no competing financial interest.

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■ REFERENCES

- (1) Kintisch, E. Climate crossroads. *Science* **2015**, *350* (6264), 1016–1017.
- (2) Bachu, S.; Gunter, W. D.; Perkins, E. H. Aquifer disposal of CO_2 -hydrodynamic and mineral trapping. *Energy Convers. Manage.* **1994**, *35*, 269–274.
- (3) Edenhofer, O. King Coal and the queen of subsidies. *Science* **2015**, *349* (6254), 1286–1287.
- (4) Gislason, S. R.; Oelkers, E. H. Carbon Storage in Basalt. *Science* **2014**, *344* (6182), 373–374.
- (5) Tollefson, J. Pilot projects bury carbon dioxide in basalt. *Nature* **2013**, *500* (7460), 18–18.
- (6) McGrail, B. P.; Schaeff, H. T.; Ho, A. M.; Chien, Y. J.; Dooley, J. J.; Davidson, C. L. Potential for Carbon Dioxide Sequestration in Flood Basalts. *J. Geophys. Res.* **2006**, *111*, B12.
- (7) Schaeff, H. T.; McGrail, B. P.; Owen, A. T. Carbonate mineralization of volcanic province basalts. *Int. J. Greenhouse Gas Control* **2010**, *4* (2), 249–261.

(8) Gislason, S. R.; Wolff-Boenisch, D.; Stefansson, A.; Oelkers, E. H.; Gunnlaugsson, E.; Sigurdardottir, H.; Sigfusson, B.; Broecker, W. S.; Matter, J. M.; Stute, M.; et al. Mineral sequestration of carbon dioxide in basalt: A pre-injection overview of the CarbFix project. *Int. J. Greenhouse Gas Control* **2010**, *4* (3), 537–545.

(9) Gruber, C.; Zhu, C.; Georg, R. B.; Zakon, Y.; Ganor, J. Resolving the gap between laboratory and field rates of feldspar weathering. *Geochim. Cosmochim. Acta* **2014**, *147*, 90–106.

(10) Fischer, C.; Arvidson, R. S.; Luetge, A. How predictable are dissolution rates of crystalline material? *Geochim. Cosmochim. Acta* **2012**, *98*, 177–185.

(11) White, A. F.; Brantley, S. L. The effect of time on the weathering of silicate minerals: why do weathering rates differ in the laboratory and field? *Chem. Geol.* **2003**, *202* (3–4), 479–506.

(12) McGrail, B. P.; Spane, F. A.; Amonette, J. E.; Thompson, C. R.; Brown, C. F. Injection and Monitoring at the Wallula Basalt Pilot Project. *Energy Procedia* **2014**, *63*, 2939–2948.

(13) Matter, J. M.; Kelemen, P. B. Permanent storage of carbon dioxide in geological reservoirs by mineral carbonation. *Nat. Geosci.* **2009**, *2* (12), 837–841.

(14) Burton, M.; Bryant, S. L. Surface dissolution: Minimizing groundwater impact and leakage risk simultaneously. *Energy Procedia* **2009**, *1* (1), 3707–3714.

(15) Matter, J. M.; Stute, M.; Snæbjörnsdóttir, S. Ó.; Oelkers, E. H.; Gislason, S. R.; Aradóttir, E. S.; Sigfusson, B.; Gunnarsson, I.; Sigurdardóttir, H.; Gunnlaugsson, E.; et al. Rapid carbon mineralization for permanent disposal of anthropogenic carbon dioxide emissions. *Science* **2016**, *352* (6291), 1312–1314.

(16) Schaef, H. T.; McGrail, B. P.; Owen, A. T. Basalt Reactivity Variability with Reservoir Depth in Supercritical CO₂ and Aqueous Phases. *Energy Procedia* **2011**, *4*, 4977–4984.

(17) Dreybrodt, W. Evolution of the isotopic composition of carbon and oxygen in a calcite precipitating H₂O–CO₂–CaCO₃ solution and the related isotopic composition of calcite in stalagmites. *Geochim. Cosmochim. Acta* **2008**, *72* (19), 4712–4724.