Final Report

Impact of Microstructure on the Containment and Migration of CO_2 in Fractured Basalts

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Abstract

The overall objective of the project was to advance the scientific and technical understanding of fracture microstructure on the flow and mineralization of CO_2 injected into fractured basalt. The project combined bench-scale CO_2-water-rock testing, geochemical characterization of rock cores, and advanced characterization of the evolution of fracture structure and carbon trapping mechanisms. A series of natural and artificial basalts were acquired and characterized for use in experiments. High pressure and high temperature experiments were performed in both batch modes and in flow-through systems. The dissolution of silicate minerals in the basalts was tracked, and the timing, identity and location of carbonate minerals that trap that added CO_2 were determined. A reactive transport model was developed that generated simulations that were consistent with the major trends in the experimental data. Novel X-ray computed tomography and nuclear magnetic resonance tools were developed as part of the project. The project found that the formation of carbonate minerals in basalts subjected to injection of CO_2-rich aqueous solutions can be rapid and extensive. The mineral trapping rate and capacity of porous basalt is much greater than that of sandstone reservoirs. Geochemical gradients that develop upon the exposure of basalt to CO_2-rich aqueous solutions lead to spatial localization of carbonate minerals in confined environments (e.g., narrow fractures, dead-end fractures, and vesicles). While carbonate minerals form in dead-end fractures, they do not form in ways that inhibit subsequent carbonation of the basalt.

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Executive Summary

Project Motivation.

Continental flood basalts are extensive geologic features currently being evaluated as reservoirs suitable for long-term storage of carbon emissions. Favorable attributes of these formations for containment of injected carbon dioxide (CO_2) include high mineral trapping capacity, unique structural features, and enormous volumes. Because the available pore volume for carbon storage in basalts is primarily in fractures, there was a need to understand the behavior of CO_2 in these reservoirs. New information was needed to determine the factors governing the extent to which coupling between mineral trapping and transport in fractured basalts enhances or inhibits the overall efficiency of carbon sequestration, and to find conditions favorable for GCS.

Project Objectives.

The overall objective of the project was to advance the scientific and technical understanding of fracture microstructure on the flow and mineralization of CO_2 injected into fractured basalt. Specific objectives were set for each year of the three-year projects. Objectives for Year 1 were to (a) develop a library of basalts, (b) demonstrate the integration of bench-scale experiments with analytical techniques, and (c) develop experimental systems with confining pressure. Objectives for Year 2 were to (a) systematically investigate properties of fractured basalts to determine extents and mechanisms of carbon sequestration, (b) evaluate the effects of confining pressure on fracture filling or opening, (c) create data packages for reactive transport modelers, and (d) develop flow-through systems for fractured basalt experiments. Objectives for Year 3 were to (a) examine impacts of dissolution-precipitation on permeability, (b) estimate storage capacity of fractured basalts, (c) demonstrate the application of advanced characterization tools, and (d) populate data packages for reactive transport modelers.

Research Approach.

The project combined bench-scale CO_2-water-rock testing, geochemical characterization of rock cores, and advanced characterization of the evolution of fracture structure and carbon trapping mechanisms. Three different natural basalt samples were used in this study: an olivine-rich basalt from the Columbia River Flood basalt, an olivine-poor/serpentinized basalt from Colorado, and a silica-rich basalt from the Grand Ronde formation that is similar to the formation of the Wallula, WA pilot-scale CO_2 injection. The basalts were prepared as 1-inch cores with reproducible fracture paths to explore reactions in advective flow paths and in dead-end fractures.

Experiments were performed with the basalt materials reacted at elevated temperatures (up to 150°C) and elevated pressures of CO_2 (up to 100 bar). Experiments that focused on the formation of carbonates in dead-end fractures included batch experiments and flow-through experiments with patterns that included branches that served as dead-end fractures. Experiments with advective flow provided information on the rates of element release from the dissolution of the minerals that constituted the basalts. Water samples were measured at regular intervals. The basalts were thoroughly characterized before and after reactions by X-ray computed tomography (CT), scanning electron microscopy, optical microscopy, Raman spectroscopy, nuclear magnetic resonance (NMR) spectroscopy, and X-ray diffraction. Selected samples were examined in real-time using novel CT and NMR systems.

A reactive transport model was developed and used to aid in the interpretation of experimental results and to explore the impacts of flow conditions and basalt heterogeneity on mineral carbonation. The model was developed in CrunchTope and used published reaction rate equations for individual minerals.

Results and Discussion.

In batch experiments with both the serpentinized and unserpentinized basalts reacted at 100°C and 100 bar CO_2, mineral carbonation in fractures was observed as early as six weeks. Zones of elevated carbonate abundance did not completely seal the fracture, and continued formation of carbonates was still occurring after 40 weeks. The experimental results were consistent with the predictions from the reactive transport model. For samples of the Grand Ronde basalt reacted at 100°C and 100 bar CO2, carbonate minerals had formed within weeks. These data enabled estimates of a carbon mineral trapping rate of 1.24 ± 0.52 kg CO_2/m^3 basalt·year and a total mineral trapping capacity of 47 kg CO_2 per cubic meter of basalt. Parallel experiments with powders, polished rock faces, and sintered pure minerals yielded additional valuable information regarding particular aspects of the mineral trapping process.

Flow-through experiments with basalt cores provided information on the rates of dissolution of the silicate minerals present in each basalt and the influence of temperature and salinity on the reaction rates. Increased temperature (from 45 to 100 °C) and salinity enhanced dissolution in flow-through experiments, and greater congruency in silicate dissolution was observed at higher temperature.

Experiments with fracture patterns that included one main advective flow path and multiple branches that acted as dead-end fractures yielded insights into the timing and location of carbonate mineral formation. At 100 °C and 6.3 mM $NaHCO_3$, representative of typical reservoir conditions, carbonate precipitates were highly localized on reactive mineral grains contributing key divalent cations. Geochemical gradients promoted localized reaction fronts of secondary precipitates that were consistent with 2D reactive transport model predictions. Increasing $NaHCO_3$ to 640 mM dramatically enhanced carbonation in diffusion-limited zones, but an associated increase in clays filling advection-controlled flow paths could ultimately obstruct flow and limit sequestration capacity under such conditions.

We developed an apparatus for in-situ nuclear magnetic resonance (NMR) studies of chemical reactions of dissolved (CO_2)-C-13 with minerals (rock or powder) under continuous flow. The system was tested with a pure forsterite pellet that could track the transformation of aqueous CO_2 into dissolved bicarbonate and ultimately into solid magnesium carbonate. In a related batch probe we used solid-state NMR of ^{29}Si and ^{13}C to monitor the reaction of forsterite with isotopically-enriched $^{13}CO_2$.

Conclusions

- The formation of carbonate minerals in basalts subjected to injection of CO_2-rich aqueous solutions can be rapid and extensive. The mineral trapping rate and capacity of porous basalt is much greater than that of sandstone reservoirs.
- Basalts with larger modal volumes of pyroxene should be considered as target minerals for carbon sequestration in basalt reservoirs, and olivine presence may be less critical than originally anticipated for sustaining mineral trapping.
- Geochemical gradients that develop upon the exposure of basalt to CO_2-rich aqueous solutions lead to spatial localization of carbonate minerals in confined environments (e.g., narrow fractures, dead-end fractures, and vesicles).
- While carbonate minerals form in dead-end fractures, they do not form in ways that inhibit subsequent carbonation of the basalt.

1. Introduction

1.1 Project Motivation and Significance

Geologic carbon sequestration (GCS) is a promising strategy for mitigating the impacts of anthropogenic CO_2 emissions on global climate change. The ultimate fate of injected carbon includes free supercritical CO_2 trapped within pores and beneath capping formations, dissolved CO_2, and carbonate minerals formed upon CO_2-water-rock reactions (DePaolo and Cole, 2013; IPCC, 2005a; Jun et al., 2013). Most geologic systems currently used or proposed for carbon sequestration are sandstone and carbonate saline aquifers a (IPCC, 2005a; Kevitiyagala, 2012). These systems are attractive because they have porosity and permeability that facilitate injection of CO_2, but they have limited capacities for mineral trapping because of the low contents of silicate minerals that contain the Ca, Mg, and Fe necessary for carbonate mineral formation. However, Fe- and Mg-rich (mafic) basalt and peridotite formations are target systems that can provide extensive mineral carbonation (Bearat et al., 2006; Matter and Kelemen, 2009a; Matter and Kelemen, 2009b; McGrail et al., 2006; Power et al., 2013; U.S. Department of Energy, 2013). CO_2 mineral trapping in basalt reservoirs can occur on timescales of two years or less as compared to hundreds or thousands of years in sandstone (Snæbjörnsdóttir et al., 2017). In the pilot-scale CO_2 injection into basalt in Iceland, 95 % of injected CO_2 mineralized to calcite within 2 years (Matter et al., 2016). In a pilot-scale injection into a basalt formation near Wallula, Washington, United States, mineralization of injected CO_2 to ankerite nodules was observed in 2-year post-injection monitoring (McGrail et al., 2017). The majority of exposed reactive surfaces in basalts are located along fractures. Our limited understanding of the extent and mechanisms of carbon sequestration in fractured basalts posed challenges to accurately estimating the storage capacity of fractured basalts and ultimately to ensuring GCS security.

The transport of fluids in fractured basalts can be controlled by the coupling of transport processes with geochemical reactions. Near the injection well, the dissolution of CO_2 produces carbonic acid, which decreases the pH and accelerates mineral dissolution (IPCC, 2005a; Kaszuba et al., 2013; White et al., 2005). The carbonic acid is neutralized by the dissolution of Ca- and Mg-containing minerals, and the dissolved calcium and magnesium released from the minerals combined with the higher carbonate concentration in the water can result in the precipitation of carbonate minerals (i.e., $MgCO_3$, $CaCO_3$). This precipitation can provide a stable sink for sequestering the injected carbon, but it can also influence advective and diffusive transport processes that are critical to successful carbon storage. Precipitates may fill fractures and impede advective fluid flow or block unreacted surfaces in fractures that are accessible only by diffusion (Power et al., 2013). Conversely, the formation of carbonate minerals in olivine-rich rocks may be self-enhancing due to the formation of new fractures induced by the volume expansion associated with carbonate precipitation (Kelemen and Hirth, 2012; Kelemen and Matter, 2008). New information was needed to determine the factors governing the extent to which coupling between mineral trapping and transport in fractured basalts enhances or inhibits the overall efficiency of carbon sequestration, and to find conditions favorable for GCS.

Because the available pore volume for carbon storage in basalts is primarily in fractures, there was a need to understand the behavior of CO_2 in these reservoirs. Further, the dissolution of silicate minerals and precipitation of carbonate minerals can influence the fracture network in ways that may either enhance or inhibit the overall sequestration capacity. A gap remained between pilot-scale field projects for which direct examination of processes and fracture structure is not possible and well-mixed laboratory-scale experiments that do not account for field-relevant fracture structures and fluid-flow. Through the use of laboratory experiments at the meso-scale, our study was designed to bridge this gap.

1.2 Project Objectives

The overall objective of the project was to advance the scientific and technical understanding of fracture microstructure on the flow and mineralization of CO_2 injected into fractured basalt. Specific objectives were to:

- Develop a library of natural and artificial basalts with a range of representative mineral contents and fracture microstructures.
- Demonstrate the ability of the integration of bench-scale experiments with an array of characterization tools to identify the locations, amounts, and types of carbonate mineral trapping in fractured basalts.
- Develop laboratory-scale system for evaluating CO_2-rich fluid interactions with fractured basalts held under confining pressure.
- Systematically evaluate the effects of basalt composition and fracture roughness and aperture on the extent and mechanisms of carbon sequestration in diffusion-limited zones using an array of techniques that includes *in situ* monitoring of fracture structure and carbon speciation using advanced nuclear magnetic resonance (NMR) and X-ray computed tomography (CT) tools.
- Quantify the extent to which confining pressure controls the propagation of fractures in basalts upon reaction with injected CO_2.
- Develop laboratory-scale equipment for NMR and CT of pressurized systems with advective flow.
- Examine the impacts of mineral precipitation and new fracture development on the permeability of fractured basalt to CO_2-rich fluids.
- Estimate the storage capacity of fractured basalts as a function of mineral content and fracture network structure, and quantify the extents of storage achieved by different trapping mechanisms.
- Demonstrate the application of advanced NMR and CT tools to fractured basalts with flow.
- Develop data packages that can be used for reactive transport model development.

2. Experimental Methods

The specific experimental methods have already been presented in two technical reports for the static experiments (Wells et al., 2017a) and for the flow-through experiments (Menefee et al., 2017a) and in a report on the library of basalts studied (Wells et al., 2016). A brief overview of the methods is provided here, and readers are referred to the technical reports for additional details.

2.1 Basalt Materials Used

Three different natural basalt samples were used in this study. An olivine-rich basalt from the Columbia River Flood basalt (Wards Scientific), an olivine-poor/serpentinized basalt from Colorado (Wards Scientific), and a silica-rich basalt from the Grand Ronde formation (DC-6 well in the Hanford archives at Pacific Northwest National Laboratory). A standard thin-section was made of each sample and examined using an electron microprobe (JEOL JXA-8200).

Backscatter (BSE), energy dispersive spectroscopy (EDS), and wavelength dispersive spectroscopy (WDS) analysis was used to determine the mineralogy present in each sample. All three samples contain fine grans of olivine, Ca-rich pyroxene, and plagioclase within a glassy matrix; however, the Grande Ronde basalt samples contain numerous vesicles.

Two synthetic materials were made to ensure the lowest amount of iron possible for NMR experiments: a pure forsterite, and an olivine-rich basalt. Two geometries were used for the in-situ static NMR probe. Forsterite samples were cold-pressed using a 6 mm diameter, and a 13 mm diameter die mold. Olivine-rich basalt samples were made by crushing, milling, and then mixing synthetic forsterite, and natural labradorite and diopside grains. A single 6 mm core was then cold-pressed. After samples were cold-pressed, each core was vacuum-sintered at 1300 °C under a vacuum of less than 10^{-5} torr for 48 h to ensure grain boundary sintering. Additional compositional and microstructural descriptions of the natural and synthetic samples can be found in the 2016 report of Wells et al. (2016).

Basalt bulk rocks were sliced into 42-45 mm thick slabs by a lapidary saw. A drill press (Dayton) with a 1-inch diamond core drill was used on the rock slabs to make multiple 1-inch cores. Basalt cores were cut into halves with a precision saw (Buehler, IsoMet 1000) with a diamond blade. For static experiments, on the surface of one half, a 100 µm deep 11 mm wide straight groove was milled in the middle via a milling machine (Roland Model MDX-40a) with a 0.5 mm diamond bur. The surface of the other half cylinder was etched with one of the three customized patterns via a milling machine (Roland Model MDX-40a) with a 0.5 mm diamond bur. The etched surface was then polished with 400 grit sandpaper until the pattern depth reach the target of 95-105 µm. When putting the two half cylinders together, the grooves serve as a fracture inside a rock core. The core with a straight groove provided a large surface area for the static batch experiments. These cores were put together and coated with epoxy (MasterBond EP42HT-2) on the outer and the bottom surface, only exposing the top ends, which mimicked a dead-end microfracture in basalt. For flow-through experiments, the pattern was one of two paths that allowed advective flow either with or without branches that served as dead-end fractures.

In addition to the cores with milled fracture paths, separate cores had fractures induced under axial stress. For this fracture preparation, cores were polished to fit two jackets. A single saw cut was made on the end of the core to guide the press bit. A hand-crank press was used to slowly induce a fracture within the core. Pressure was applied long enough to generate a fracture, but not so long as to completely fracture the core into two pieces. Resulting samples contain a fracture with an opening less than 1 mm wide, that extends approximately half way down the core from the top. As a result of the fracturing process, each fracture has a slightly different geometry.

2.2 Batch Experiments with Fractured Basalts

Multiple cores were placed on a core holder, which fit in a PTFE liner that was put into the 600 mL stainless steel high pressure reactor (Parr Instrument). Ultrapure water was added in a ratio of 64 mL per core to fully immerse all the cores in the reactor. A syringe pump (500D, Teledyne Isco) provided a constant CO_2 pressure (100 bar) to the headspace. The reactor was heated to 100 °C or 150 °C. After reacting for 6, 12, 20, 30 and 40 weeks, the reactor was cooled and degassed and one core was collected. Meanwhile 64 mL solution was removed from the reactor to keep the water to solid ratio a constant. Liquid sample from the 64 mL solution removed was filtered and acidified to 1% HNO_3 concentration. The reactor was reheated and repressurized to the previous conditions and kept reacting.

Two complementary experiments were conducted using core samples containing a milled flow path with four dead-end fractures. The first was completed in the flow-through setup at the University of Michigan. CO_2 was first equilibrated with a brine solution containing DI water and 6.3 mM $NaHCO_3$ in a batch reactor (Parr Instruments) at 100 °C and 100 bar PCO_2. The core sample was encased in heat shrink tubing and inserted into a viton sleeve, which was then placed in a biaxial flow-through reactor (Core Laboratories) under 300 bar confining stress. The reactor was heated to 100 °C using a beaker heater jacket connected to a temperature controller (BriskHeat) that maintained temperature within ±1°C of the set point. CO_2-equilibrated brine was then injected into the core sample using a high-pressure syringe pump (500D, Teledyne Isco) at a constant rate of 1 mL/h. Differential pressure was continuously monitored via pressure transducers installed upstream and downstream of the flow-through reactor. Back pressure was maintained at 100 bar using a back pressure regulator (Swagelok, Inc.) to prevent in line CO_2 degassing. Effluent samples were continuously collected over 2-hour intervals for the first 10 hours and then taken regularly every 8-10 hours (3 samples per day) over 10 days.

A semi-replicate experiment was conducted at a National Energy Technology Laboratory (NETL) facility in Morgantown, WV using a flow-through cell within an industrial CT scanner (Northstar Imaging). The same experimental conditions used in the first experiment were applied, but the experiment was run at room temperature given equipment limitations in heating the system. The sample was encased in heat shrink tubing, placed in a viton sleeve, and placed in a flow-through reactor within the scanner setup. CO_2 was first equilibrated with the brine solution (DI water + 6.3 mM $NaHCO_3$) under 100 bar PCO_2 using a standing stirred pressure reactor (Parr Instruments). The core sample was subjected to 300 bar confining pressure and the fluids were injected at a constant rate of 1 mL/h using a high-pressure syringe pump. Another syringe pump was used to maintain a constant back pressure of 100 bar, which precluded effluent sampling at the outlet. To avoid the risk of pressure loss associated with a bypass valve, effluent samples were taken from a micro-metering valve located downstream of the reactor and averaged over 3-hour intervals to attain sufficient fluid for analysis. The duration was extended to 18 days to help compensate for the anticipated reduction of mineral reactivity associated with lower temperatures. xCT scans were taken every 24 hours and reconstructed using proprietary software (North Star Imaging).

2.3 Flow-through Experiments with Fractured Basalts

Flow-through experiments conducted at the University of Michigan were carried out using a biaxial core holder with working pressures up to 6,000 psi (41 MPa) (Core Laboratories). Fluids were first equilibrated with CO_2 in a batch reactor (Parr instruments) at the experimental temperature and pressure for 24 hours prior to initiating flow. A 500-mL syringe pump (Teledyne Isco) was used to maintain a constant CO_2 pressure in the headspace. Core samples were secured in chemical-resistant heat shrink tubing to prevent movement and placed in a viton sleeve within the core holder. A confining pressure of 20 MPa and pore pressure of 10 MPa were used in all experiments conducted here. The system was heated to the experimental temperature using beaker heaters connected to a temperature control box (BriskHeat) to maintain *in situ* temperatures within ±1°C of the set point. After achieving experimental temperature and pressure conditions, the pre-equilibrated CO_2-acidified fluid was transferred from the batch reactor to a 500-mL syringe pump and injected into the core sample at the experimental flow rate. System pressure was maintained with a back pressure regulator, and system pressure was continuously logged via pressure transducers installed upstream and downstream of the core.

Effluent samples were collected over regular intervals from a flow line downstream of the back pressure regulator and subsequently analyzed for major cations and anions.

The flow-through system at the National Energy Technology Laboratory (NETL) in Morgantown functioned similarly to the system at Michigan, but was set up in a climate-controlled room equipped with an industrial X-ray computed tomography (CT) scanner (Northstar Imaging) to allow for real-time 4D imaging. Due to technical difficulties in heating the system, a low-temperature experiment (room temperature, 20°C) was conducted using a serpentinized basalt core with the multi-path advection and diffusion design. The influent brine (6.3 mM $NaHCO_3$) was first equilibrated with CO_2 (10 MPa) in a batch mixing vessel. A "dry" pre-scan of the core was taken before placing it in the core holder for the experiment. The CO_2-acidified fluid was then injected through the sample using dual syringe pumps (Teledyne Isco). System back pressure was also maintained using dual syringe pumps, and effluent samples were collected from a micrometering valve downstream of the core holder. Pressure was logged continuously from transducers upstream and downstream of the core sample. Once CO_2-acidified fluid broke through to the core sample, an initial (0 hr) scan was taken. The core was scanned about once every 24 hours for the duration of the experiment, which was extended to 18 days in an attempt to compensate for the significant reduction in reactivity associated with lower than originally hoped for temperature.

2.4 Analysis of Samples

2.4.1 Aqueous Samples. Aqueous samples from batch experiments were analyzed by inductively coupled plasma mass spectrometry (ICP-MS, Agilent model 7500ce) for cations and aqueous silica. Anions were quantified using ion chromatography (Theromo Scientific, DIONEX ICS-1600). Effluent samples from both flow-through experiments were analyzed via ICP-MS to measure major cation concentrations (Ca, Mg, Fe, Si, Al, Na, and K). Samples were acidified to 2% HNO_3 prior to analysis in an ICP-MS system at the University of Michigan (7900 Agilent Technologies, CA). Due to the high Na concentrations in the influent brine, measured concentrations were inconsistent and are not reported in the results.

2.4.2 Solid-Phase Characterization. Selected core samples for batch experiments were scanned by X-ray computed microtomography before reaction (Scanco uCT40) and after reaction (Zeiss Xradia Versa 520). The basalt cores were cut open. The surface of the straight groove was examined by an optical microscope (LEICA, DFC295) to search for precipitates. The precipitates were then scanned via Raman spectroscopy (HoloLab Series 5000 Laser Raman Microprobe, Kaiser Optical) with a 532 nm laser. Scanning electron microscopy with energy-dispersive X-ray spectroscopy (SEM-EDX, FEI Nova 230) was applied to examine the precipitate morphology and elemental composition. The precipitates were identified by both Raman spectroscopy and SEM-EDX. Point counting was conducted via a point counting station (LEICA, DM2700p) to semi-quantitatively analyze the precipitate distribution on the surface. The number of observable precipitates was counted in every 100-μm wide step across the fracture surface. Point counting was performed along lines at 1, 3, 5, 7 ,10, 15, 20…35 mm below the open end of the fracture.

2.5 Reactive Transport Modeling

All models were developed in CrunchTope, a multicomponent reactive transport code that has been applied to a variety of environmental problems involving flow through porous media (Steefel et al., 2015). Simulations were conducted using the global implicit approach (GIMRT), where time steps are extended as the system approaches steady state to enhance computational efficiency. Additional details on the code's capabilities, limitations, and governing equations are available in the user's manual (available for download from www.csteefel.com).

Mineral reactions are modeled based on transition state theory assuming continuous reversibility between dissolution and precipitation at equilibrium. Reaction rate constants at 100°C, the temperature applied in all models considered here, were calculated based on selected literature values for the reaction rate constant at 25°C and activation energy according to the Arrhenius relationship. Reaction pH dependence was incorporated by summing adjusted rate constants for acid (H), neutral (neu), and basic (OH) mechanisms. Dolomite was intentionally excluded as a secondary mineral due to its well-established disinclination to precipitate under modern natural conditions despite thermodynamic favorability. Quartz was also suppressed due to its slow precipitation kinetics. Under the conditions in this study, solutions supersaturated with respect to SiO_2 would predominantly precipitate amorphous silica, which has a lower interfacial energy and faster nucleation rate than crystalline forms.

2.6 Experiments with High Pressure NMR Probes

2.6.1 Batch NMR Probe. A high-pressure single-channel NMR probe capable of observing liquids, gases, supercritical fluids and solids was constructed. An elevated-temperature, elevated-pressure sample holder was used (fabricated out of zirconia). The NMR electronics are comprised of an RLC circuit--a "tank circuit", using an Alderman-Grant coil, which is tuned to 89.07 MHz for ^{13}C in a "354 MHz" magnetic field (referring to the proton resonance frequency). The high-pressure reaction vessel was made of yttria-stabilized zirconia called AmZirOx 86 (sold by AstroMet Inc. Cincinnati, Ohio). It can hold up to 400 bar of pressure and is rated to 400 °C. The reaction vessel has advantages that include being non-conductive, having a high-tensile strength, containing no carbon, remaining unreactive to most chemicals, and being impermeable to gas with 0% water retention.

The NMR coil is set to 0.5-inch above the bottom of the reaction vessel to reduce susceptibility inhomogeneity caused by position at the bottom of the tube within the correctional range of the shims. The temperature in the probe is monitored via two Type K thermocouples. One is in the (heated zone of probe) to monitor reaction vessel temperature, and the other is near the variable tuning capacitor to monitor the temperature of NMR circuitry in the cool zone of the probe. The high-pressure tubing and associated valves, tuning rods of capacitors, thermocouple wire, RF cable and cooling tubes are fed from the top of the probe. The air heating tube and vent tube are from the bottom of the probe. Heating was accomplished by flowing heated air to the region within the probehead – the sample measurement space. Cooling air is blown separately (and is not shown in the diagram) over the temperature sensitive variable tuning capacitors and protects form overheat or damage (max operating temperature of 125 °C). The pressure in the probe is monitored via an MSP-300 pressure transducer (Measurement Specialties Inc.).

High pressure $^{13}CO_2$ was created by cryogenic pressurization. A high-pressure collection vessel was submerged in liquid nitrogen (LN2) to freeze $CO_{2(g)}$ from a conventional (medium-pressure) cylinder. After an amount of CO_2 is frozen inside the vessel, it is subsequently allowed to warm to room temperature, thereby creating elevated pressure in the probe and sample space. A target pressure is reached once the system reaches equilibrium and excess CO_2 is vented. A safety valve is also installed on the manifold with a breaking pressure of 3625 psi to ensure the manifold as a whole does not become over-pressurized, beyond the ratings of various components.

2.6.2 Flow-through NMR Probe. The flow-through, elevated-pressure and -temperature NMR apparatus consists of four main interconnected parts: a gas manifold, a gas and solution mixing vessel, a flow pump, and a NMR probe. The design and testing of the probe is presented in a peer-reviewed publication in NMR spectroscopy literature (Sesti et al., 2017). The gas manifold was assembled using commercial components for the purpose of delivering CO_2, and potentially gas mixtures, to the mixing vessel. A high-pressure liquid-gas mixing vessel was fabricated for the purposes of providing a reservoir for mixing liquids and one or more gases at elevated pressures. The vessel was machined from titanium, and its 10 mL volume capitalizes on a broad diameter that permits a high surface area between liquid and gas layers to quickly reach equilibrium between these two phases. To avoid corrosion by these acidic solutions, the base and O-ring-sealed cap were made of a titanium alloy (6Al-4V). There are two ports on the top cap: one is for the introduction of gas into the vessel, and the other is for returning solution to the mixing vessel after passing through the NMR probe. Temperature regulation is carried out through a cartridge heater (Omega) in the base of vessel, which is controlled by a temperature controller. The temperature controller was linked to a type-T thermocouple placed as shown. The flow pump is a HPLC-style pump (Waters 6000). The pump has an operating pressure range of 0-414 bar and a flow rate from 0.1 to 9.9 ml/min with variability in 0.1 ml/min increment. The solution comes to the pump from the base of mixing vessel, and the output goes into the sample space of the NMR probe, notably outfitted so that this can be accomplished while the probe is inside the magnet.

The high-pressure single-channel, elevated-temperature and pressure NMR probe is "home built" and capable of observing liquids, gases, supercritical fluids and solids. The sample holder is fabricated from zirconia. The NMR electronics are comprised of a tuned circuit and a radio-frequency (RF) solenoid coil, which is tuned to 89.07 MHz for ^{13}C in a 8.3 Tesla external magnetic field (equivalently a "~350 MHz" instrument, referring to the proton resonance frequency). The high-pressure reaction vessel within the coil was made of yttria-stabilized zirconia called AmZirOx 86 (sold by AstroMet Inc. Cincinnati, Ohio). It has a 1.2 cm outer diameter and 0.66 cm inner diameter. To contain the high-pressure environment, two titanium alloy (6Al-4V) plates are used on either end, held together with two titanium alloy screws. The assembly can hold up to 400 bar of pressure and is rated to 400 °C. Temperature control in the sample space is accomplished by flowing heated air into the coil region. Cooling air is blown separately (and is not shown in the diagram) over the temperature-sensitive variable tuning capacitors to protect them from overheating or damage (since the maximum operating temperature is 125 °C).

3. Results and Discussion

Detailed presentation and discussion of the projects results has been provided in technical reports (Menefee et al., 2017a; Wells et al., 2017a) and in peer-reviewed publications submitted by the project team. The following sections highlight key results and their implications for carbon sequestration, and these sections specifically note the references in which additional detailed results and discussion can be found.

3.1 Carbon Mineralization and Basalt Dissolution in Static Experiments

3.1.1 Experiments with Basalt Cores. For cores of basalt, we first studied flood basalt and serpentinized basalt with engineered fractures that were reacted in water equilibrated with 10

MPa CO_2 at 100˚C or 150˚C for up to 40 weeks (Xiong et al., 2017b). Carbonation in basalt fractures was observed as early as 6 weeks with Mg- and Ca-bearing siderite formed in both basalts reacted at 100˚C and Mg-Fe-Ca carbonate minerals formed in the flood basalt reacted at 150˚C. X-ray µCT segmentation revealed that precipitates filled 5.4% and 15% (by volume) of the flood basalt fracture after 40 weeks of reaction at 100˚C and 150˚C, respectively. Zones of elevated carbonate abundance did not completely seal the fracture. Limited siderite clusters (<1 % volume fraction) were found in localized areas in the serpentinized basalt fracture. The experimental results were consistent with predictions from a 1-dimensional reactive transport model developed in CrunchTope examined how geochemical gradients drive silicate mineral dissolution and carbonate precipitation in the fracture (see Section 3.4). The model predicted that siderite would form as early as 1 day after the addition of CO_2. The predicted location of maximum siderite abundance is also consistent with experimental observations, and the predicted total carbonate volumes are comparable to estimates derived from CT segmentation.

We experimentally investigated mineral carbonation in whole core samples retrieved from the Grand Ronde basalt (Xiong et al., 2018), the same formation into which ~1000 tons of CO_2 was recently injected in an eastern Washington State pilot-scale demonstration. The basalt core is porous and contains many mm- to cm-scale vesicles. The pores are residual gas bubbles that were present during basalt formation. The rate and extent of carbonate mineral formation at 100°C and 100 bar was tracked via time-resolved sampling of bench-scale experiments. Basalt cores were recovered from the reactor after 6, 20, and 40 weeks, and three-dimensional X-ray tomographic imaging of these cores detected carbonate mineral formation in the fracture network within 20 weeks. Under these conditions, a carbon mineral trapping rate of 1.24 ± 0.52 kg CO_2/m^3 basalt·year was estimated, which is orders of magnitude faster than rates for deep sandstone reservoirs. Based on these calculations and under certain assumptions, available pore space within the Grand Ronde basalt formation would completely carbonate in ~40 years, resulting in solid mineral trapping of ~47 kg CO_2 per cubic meter of basalt.

3.1.2 Experiments with Powders, Polished Rock Faces, and Sintered Pure Minerals.

In parallel with the experiments with cores of basalt rock, additional experiments were performed to examine particular aspects of the geochemical processes in greater detail. Glass tubes packed with grains of olivine or basalt with different grain sizes and compositions were used to explore the identity and spatial distribution of carbonate minerals that form in dead-end one-dimensional diffusion-limited zones that are connected to a larger reservoir of water in equilibrium with 100 bar CO_2 at 100 °C (Xiong et al., 2017a). Magnesite formed in experiments with olivine, and Mg- and Ca-bearing siderite formed in experiments with flood basalt. The spatial distribution of carbonates varied between powder packed beds with different powder sizes. Packed beds of basalt powder with large specific surface areas sequestered more carbon per unit basalt mass than powder with low surface area. The spatial location and extent of carbonate mineral formation can influence the overall ability of fractured basalt to sequester carbon.

We performed experiments to examine the influence of the internal pore structure and grain boundary surfaces on the extent and locations of silicate mineral dissolution and carbonate mineral precipitation in dense aggregates (Wells et al., 2017c). We conducted several experiments at 100 °C and 100 bar CO_2 using sintered San Carlos olivine (Fo_{90}) and pure forsterite (Fo_{100}) cylinders, and we documented the type and spatial distribution of the reaction products. Timing of carbonation was measured using in-situ ^{13}C NMR spectroscopy without removing the sample from the reactor. Ex-situ solid-state NMR spectroscopy, Raman spectroscopy, and electron microscopy were used to examine reacted samples and precipitates. Within 15 days, magnesite is observed only on the surface of Fo_{90}. After 53 and 102 days of reaction, magnesite and amorphous silica are observed as a crust around the entire Fo_{100} cylinder and as isolated layers within the sample. The spatial transition from an amorphous silica layer to the host Fo_{100} indicates that the development of amorphous silica did not impede further forsterite dissolution. While earlier studies documented localized reactions at the grain scale, the development of distinct zones of magnesite and amorphous silica suggest that divalent metal cations are mobile during carbonation of olivine. Grain boundaries, pore structure, and geochemical gradients strongly influence the locations of silicate mineral dissolution and carbonate mineral precipitation even in the absence of advective transport or confinement. The clear spatial distribution of precipitates observed in this study indicates that carbonation in heterogeneous reservoirs may be strongly affected by grain-scale microstructure.

We examined basalt surfaces as dissolution progressed to gain important information about which minerals are dissolving, the timing and sequence of dissolution, and the effects these processes have on surface roughness and morphology (Wells et al., 2017b). We carried out two series of experiments using two polished Columbia River flood basalt samples in CO_2-rich water at 150 °C and 100 bar to observe the physical and geochemical changes during dissolution. Scanning electron microscopy, 2D profilometer analysis, and 3D laser confocal microscopy were combined with ICP-MS to characterize dissolution. Dissolution resulted in pitting, dissolution along fractures and grain boundaries, and an increase in species concentrations in the bulk solution over incremented reaction times. Based on these observations, early dissolution of olivine grains contribute Mg^{2+} and Fe^{2+} to aqueous solution in initial stages (less than 1 week at a pH < 4), while slower continuous dissolution of Ca-rich pyroxene contributes Mg^{2+}, Fe^{2+}, and Ca^{2+} to the bulk solution over a longer period of time. The complete dissolution of olivine grains resulted in pits up to 200 μm deep. Dissolution of plagioclase and matrix was slower and resulted in the formation of micro-sized textures (< 10 μm). Following 1-2 months of reaction, the surface roughness parameters (mean and root mean squared) increased by factors of 42 and 28, respectively, while surface area of the flood basalt increased 20% relative to the starting polished surface. The results of this study indicated that 1) pyroxene is the sustaining contributor of divalent metal cations during dissolution of basalt and 2) the limited connectivity limits of olivine and pyroxene grains the exposure of new reactive surface areas.

3.2 Basalt Dissolution in Flow-through Experiments

A series of high temperature and high pressure (45°C and 100°C; 100 bar) experiments were conducted to examine geochemical alterations of fractured serpentinized and unserpentinized basalts exposed to high P_{CO2} fluids (Adeoye et al., 2017). Net mineral dissolution was observed in flow-through experiments that examined reactions under advection-dominated conditions, whereas carbonate mineral precipitation occurred along basalt fractures after 6 weeks of reaction in static batch experiments where mass transport was diffusion limited. Consistent with prior work, increased temperature and salinity enhanced dissolution in flow-through experiments, and greater congruency in silicate dissolution was observed at higher temperature. Analysis of the reacted cores via X-ray computed tomography revealed regions of enhanced dissolution along the fracture pathway that correspond to contact with large grains of pyroxene and olivine.

3.3 Carbon Mineralization and Basalt Dissolution in Mixed-Flow Systems

A series of high-temperature, high-pressure core flooding experiments was conducted to investigate how transport limitations, reservoir temperature, and brine chemistry impact carbonation reactions following injection of CO_2-rich aqueous fluids into fractured basalts (Menefee et al., 2018). These basalts were the ones with a main advective path and multiple branches that served as dead-end fractures. At 100 °C and 6.3 mM $NaHCO_3$, representative of typical reservoir conditions, carbonate precipitates were highly localized on reactive mineral grains contributing key divalent cations. Geochemical gradients promoted localized reaction fronts of secondary precipitates that were consistent with 2D reactive transport model predictions. Increasing $NaHCO_3$ to 640 mM dramatically enhanced carbonation in diffusion-limited zones, but an associated increase in clays filling advection-controlled flow paths could ultimately obstruct flow and limit sequestration capacity under such conditions. Carbonate and clay precipitation were further enhanced at 150 °C, reducing the pre-reaction fracture volume by 48% compared to 35% at 100 °C. Higher temperature also produced more carbonate-driven fracture bridging, which generally increased with diffusion distance into dead-end fractures. In combination, the results are consistent with field tests indicating that mineralization will predominate in buffered diffusion-limited zones adjacent to bulk flow paths and that alkaline reservoirs with strong geothermal gradients will enhance the extent of carbon trapping.

3.4 Development and Demonstration of Reactive Transport Modeling Tools

A predictive modeling framework was designed to evaluate the roles of transport limitations and mineral spatial distributions on mineral dissolution and carbonation reactions in fractured basalts exposed to CO_2-acidified fluids (Menefee et al., 2017c). Reactive transport models were developed in CrunchTope based on data from high-temperature, high-pressure flow-through experiments. Models isolating the effect of transport compared nine flow conditions under the same mineralogy. Heterogeneities were incorporated by segmenting an actual reacted core sample, and these results were compared to equivalent flow conditions through randomly generated mineral distributions with the same bulk composition. While pure advective flow with shorter retention times promotes rapid initial carbonation, pure diffusion sustains mineral reactions for longer time frames and generates greater net carbonate volumes. For the same transport conditions and bulk composition, exact mineral spatial distributions do not impact the amount of carbonation but could determine the location by controlling local solution saturation with respect to secondary carbonates. In combination, the results indicate that bulk mineralogy will be more significant than small-scale heterogeneities in controlling the rate and extent of CO_2 mineralization, which will likely occur in diffusive zones adjacent to flow paths or in dead-end fractures.

The data used to calibrate the model have been made available through the Energy Data Exchange (Menefee et al., 2017b) so that other researchers developing reactive transport models for carbon sequestration can benefit from them. These are data from a series of dissolution-driven core-flooding experiments where CO_2-acidified brine was injected through serpentinized and unserpentinized basalt cores under elevated temperature (45-100°C) and pressure (10 MPa P_{CO2}). The full data set, including error bars from triplicate measurements, are provided in the data deliverable. The "final" specific surface areas used in the models are provided along with the reaction rate constants, activation energy, and pH dependences of minerals used in modeling, most of which were taken from literature.

3.5 Development and Demonstration of NMR Tools for Carbon Sequestration Research

We developed an apparatus for in-situ nuclear magnetic resonance (NMR) studies of chemical reactions of dissolved (CO_2)-C-13 with minerals (rock or powder) under continuous flow (Sesti et al., 2017). The operating range of the apparatus is 18-150 degrees C and 1-140 bar. A flow pump is used to circulate a CO_2-water solution, with a heated mixing vessel where CO_2 gas equilibrates with a water solution. The NMR probe is built around a strong zirconia ceramic vessel, with o-ring sealed connections; the mineral is contained inside. The horizontal orientation of the zirconia vessels allows use of a radio frequency solenoid for improved spin sensitivity. The system was tested with a pure forsterite pellet that was 6 mm in diameter at a length of 13 mm containing a fracture was reacted in the probe head. It was submerged in a flowing aqueous solution of $^{13}CO_2$ (g) at a pressure of 100 bar with a temperature of 100 °C. $^{13}CO_2$ gas was added throughout the duration of the equipment to keep a constant pressure of 100 bar. A dominant CO_2 (aq) peak is seen along with a bicarbonate peak. After 7 days, the CO_2 and bicarbonate peaks are still present, but a solid carbonate powder pattern is present.

In a related batch probe we have used solid-state NMR of ^{29}Si and ^{13}C to monitor the reaction of forsterite with isotopically-enriched $^{13}CO_2$ (Cui et al., 2016). The fate of the silicon that comes from the dissolution of forsterite in the presence of water or NaCl brine was monitored as a function of depth in a packed bed reactor, which used elevated-temperature and –pressure conditions to mimic underground geological sequestration conditions. Silicon provides an important window into the reaction since the precipitation of amorphous silica can affect forsterite dissolution, and solid-state MAS NMR can readily distinguish between ^{29}Si in forsterite (Mg_2SiO_4) and amorphous silica. Furthermore difference between Q^3 and Q^4 species of amorphous silica were observed as a function of depth. Results differed between water and brine-based reactions, with enhanced dissolution of forsterite observed in the brine.

4. Conclusions

The project determined that the formation of carbonate minerals in basalts subjected to injection of CO_2-rich aqueous solutions can be rapid and extensive. The mineral trapping rate and capacity of porous basalt is much greater than that of sandstone reservoirs. Carbonate minerals have been observed upon reaction of natural basalts with the fluids in reaction times as short as six weeks, and the reactive transport model predicts carbonate formation as early as 1 day. The identity of the dominant carbonate mineral depends on the mineralogy of the particular basalt that is reacting.

Olivine is often considered as the main source for divalent metal cations in basalt formations, particularly when carbonation is the primary goal for permanent carbon storage. However, by examining dissolved cations in solution and the reacted surface area over incremented time periods, this study indicates that the slightly slower dissolution of pyroxene compared to olivine and higher modal volume act as a sustained source for several divalent metal cations (Ca^{2+}, Fe^{2+}, and Mg^{2+}) that can be used in carbonation reactions. The results of this study indicate basalts with larger modal volumes of pyroxene should be considered as the target mineral for carbon sequestration in basalt reservoirs.

Geochemical gradients that develop upon the exposure of basalt to CO_2-rich aqueous solutions lead to spatial localization of carbonate minerals in confined environments (e.g., narrow fractures, dead-end fractures, and vesicles). While the bulk mineralogy of a basalt reservoir will influence the availability of divalent cations, diffusive mass transport conditions may be required to achieve mineral sequestration of injected CO_2. Hence, it is unlikely that significant mineralization will occur near wellbores or along interconnected fracture pathways due to strong advective flow of CO_2-acidified solutions. CO_2 mineral carbonation is most likely to occur in dead-end fractures, at distances further away from the wellbore where advective forces may be less dominant, or long after injection has ceased.

While carbonate minerals form in dead-end fractures, they do not form in ways that inhibit subsequent carbonation of the basalt. The zones of maximum carbonate formation did not block the fracture and they did not prevent further mineral trapping reactions in deeper region within the fracture for the conditions of this study. The fact that carbonates formed in narrow confined fracture surfaces between the unmilled surfaces under all tested conditions indicates that basalts with low porosity and primary fracture permeability may still serve as effective repositories for CO_2 mineralization, provided injectivity is maintained near the wellbore. Furthermore, precipitation first filling the tips of dead-end fractures may allow zones of restricted flow to fully carbonate without self-sealing.

The project developed a set of tools that can benefit continuing carbon sequestration research. A reactive transport model was developed that accounts for the locations, abundances, and reaction rates of specific minerals in a basalt. The project demonstrated the value in combing X-ray computed tomography imaging, electron microscopy, and Raman spectroscopy to determine the locations, morphology, and identity of carbonate minerals that formed. A novel nuclear magnetic resonance probe was developed that can provide real-time information on carbon speciation in minerals in contact with CO_2-rich solutions while those reactions are progressing at elevated pressure and temperature.

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