

Simulation of CO₂ mineral trapping and permeability alteration in fractured basalt: Implications for geologic carbon sequestration in mafic reservoirs

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ABSTRACT

Basalt formations are potentially attractive targets for carbon capture and sequestration (CCS) on the basis of favorable CO₂-water-rock reactions, which result in permanent CO₂ isolation through mineral trapping. Recent pilot-scale experiments in Iceland and Washington state, USA, provide promising results that indicate rapid carbon mineralization occurs within basalt reservoirs. Nevertheless, transitioning these pilot-scale results to large-scale industrial CCS operations is fraught with uncertainty because fluid flow in basalt formations is governed by fracture-controlled hydraulic properties that are highly heterogeneous and difficult to map *in situ*. This uncertainty is exacerbated by feedbacks between multi-phase fluid dynamics (CO₂ and water) and fluid-rock reactions, which may result in a reinforcing feedback comprising CO₂ mineralization, permeability alteration, and fluid mobility. To begin to understand the feedbacks between multi-phase fluid flow and mineralization in fractured basalt, this study uses reactive transport simulation methods to model CO₂ infiltrating a meter-scale, synthetic basalt fracture overlying a storage reservoir while accounting for porosity change due to mineralization and its corresponding effect on permeability and fluid mobility. Results show that (i) carbonate and clay mineralization tends to occur downgradient of a fracture intersection, (ii) mineralization reduces porosity, which leads to permeability reduction and slows free-phase CO₂ migration, (iii) stronger porosity-permeability coupling increases the proportion of mineralized carbon while reducing CO₂ mass that can enter fracture, which may lead to self-sealing behavior as fluid mobility approaches nil, and (iv) errors caused by unknown porosity-permeability relationships are small in comparison to errors that arise by omitting mineralization-induced permeability reduction when simulating CO₂ sequestration scenarios in basalt reservoirs.

1. Introduction

Carbon capture and sequestration (CCS) has been proposed as a mitigation strategy for reducing anthropogenic CO₂ emissions in the energy sector (Bennion and Bachu, 2005; Metz et al., 2005). Sedimentary basins are the most common geologic environment for CCS operations, but permanent mineral trapping in such environments occurs over time scales exceeding 10² – 10³ years (Bachu et al., 1994; Mito et al., 2008; Benson and Cole, 2008). Thus, during the time interval between CO₂ injection and the time when much of the CO₂ has been sequestered in mineral phases, there is potential for reservoir leakage. Because leakage rates below 1% per thousand years are required to effectively mitigate the adverse effects of atmospheric CO₂ accumulation (Shaffer, 2010), there is a high probability that this rate of CO₂ loss will be

exceeded before mineralization occurs. In contrast, basalt formations have been shown to accommodate CO₂ mineral trapping over much shorter timescales, e.g., 10⁰ – 10¹ years (Goldberg et al., 2008; Schaefer et al., 2010; Rosenbauer et al., 2012; Gislason et al., 2010), thus rapidly immobilizing the injected CO₂ and reducing the likelihood of leakage before mineralization occurs.

Mafic and ultramafic rocks are widespread on the Earth's surface (Rudnick, 2018). Within the United States, the Columbia River Basalt Group (CRBG) covers more than 164,000 km² in Washington, Oregon, and Idaho (McGrail et al., 2006; Reidel et al., 2002), and India's Deccan Volcanic Province (DVP), covers ~500,000 km² in west-central India (Eldholm and Coffin, 2000; Tiwari et al., 2001; McGrail et al., 2006). The large volume of continental basalt provinces offers significant CO₂ storage capacity in locations that have not traditionally been considered

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viable for CCS. Moreover, CCS in continental basalt formations may provide an opportunity to mitigate the adverse effects of increasing CO₂ emissions in some developing countries (Szulczewski et al., 2012). For example, coal-fueled power plants are the major source of electricity generation in India, where 12 – 40 GW per year will be added to the current coal-fueled energy capacity from 2015 to 2025 (Shearer et al., 2017). Total annual CO₂ emissions in India were estimated as 2.24 billion tonnes (Mt) in 2017, which contributed ~7% to global CO₂ emissions, and this number will continue to increase with ongoing economic development (Le Quéré et al., 2018; Holloway et al., 2009).

Because CCS in basalt formations expands the geographic opportunities for geologic carbon storage, there is considerable interest in the processes that govern mineral trapping in basalt reservoirs (Goldberg et al., 2008; Schaef et al., 2010; Rosenbauer et al., 2012; Gislason et al., 2010). During CCS in basalt reservoirs, CO₂ dissolution in formation water releases H⁺ to drive mineral dissolution of olivine and pyroxene, which releases divalent cations (Ca²⁺, Mg²⁺, Fe²⁺) that react with dissolved CO₂ (i.e., HCO₃⁻, CO₃²⁻) to form secondary mineral phases, such as calcite, magnesite, siderite (Knauss et al., 1993; Wang and Giammar, 2013). Here, we refer to this process whereby dissolved CO₂ is removed from solution and incorporated into carbonate minerals as “carbon mineralization”. Basalts contain up to 25% combined molar concentration of Ca, Mg, and Fe (McGrail et al., 2006), and the rate of release of these cations from basalt dissolution is as much as two orders of magnitude faster than occurs in more silica-rich rocks (Wolff-Boenisch et al., 2006). For example, Hövelmann et al. (2012) presented experimental results showing that carbonate alteration products formed after 7 days of olivine exposure to CO₂ and water at 150°C. In addition, Xiong et al. (2017b) used X-ray μ CT segmentation to show that secondary alteration products filled up to 15 volume percent of the fractures in basalt after 40 weeks of exposure to an aqueous phase containing dissolved CO₂.

Two pilot-scale CO₂ injection tests have shown that mineral trapping in basalt reservoirs is feasible at the field scale. The CarbFix Project at Hellisheidi geothermal power plant in southwest Iceland injected 230 tons of aqueous CO₂ in 2012, and subsequent mass balance and tracer tests found that 95% of the injected CO₂ was mineralized within two years (Matter et al., 2016). Additionally, the Wallula Basalt Sequestration Pilot Project located in southeastern Washington, USA, injected ~1,000 metric tons of supercritical CO₂ in 2013. Analyses of post-injection sidewall cores from the Wallula site found that carbon mineralization was widespread within the injection zone (McGrail et al., 2017). These two CO₂ injection projects have successfully demonstrated the feasibility of mineral trapping in basalt reservoirs; however, many uncertainties concerning the mineralization process and relationship between mineralization and fluid flow behavior remain to be investigated before these same approaches can be applied in industrial-scale projects.

To understand the feasibility of industrial-scale CCS operations in basalt reservoirs, a number of recent modeling studies have shown that free-phase CO₂ may become physically trapped over the rapid timescales (10⁰ – 10¹ yr) required to allow for permanent CO₂ isolation through mineralization processes in basalts (Jayne et al., 2019a; Jayne et al., 2019b; Pollyea et al., 2014; Pollyea and Fairley, 2012). However, these studies neglect fluid-rock reactions, which precludes analysis of physical and chemical feedbacks associated with CO₂ injection into basalt formations, as well as their long-term mineral trapping characteristics. In contrast, Aradóttir et al. (2012) utilized reactive transport simulation to show that geologic conditions at the CarbFix site are conducive to mineral trapping, but this study did not include the complex fracture heterogeneity associated with basalt reservoirs. Moreover, the CarbFix project injects aqueous phase CO₂, so feedbacks between multi-phase fluid processes and CO₂ mineralization were not considered.

Several recent studies provide insights into the nature of free-phase CO₂ infiltrating a basalt fracture network. At the outcrop scale, Gierzynski and Pollyea (2017) simulated supercritical CO₂ migrating

vertically from a high-permeability basalt reservoir into an overlying low-permeability basalt flow interior. Utilizing stochastic simulation methods, this study found that free-phase CO₂ tends to accumulate at the fracture intersections because relative permeability effects decrease downgradient (advective) CO₂ mobility when a single fracture branches into one or more diverging fractures (Fig. 1). While this study did not consider fluid-rock reactions and CO₂ mineralization, these results are congruent with a number of core-scale experiments that show carbonate minerals are likely to form in diffusion-dominated areas of a fracture, where flow rates are small and the Damköhler number is large (Adeoye et al., 2017; Luhmann et al., 2017a; Xiong et al., 2017a). For example, Adeoye et al. (2017) used batch reactor experiments to show that carbon mineralization is common at the dead-end of fractures, where advection is less dominant. Both Luhmann et al. (2017b) and Andreani et al. (2009) also found that mineral precipitation alters basalt fracture permeability in diffusion-controlled regions of a fracture. This relationship implies that carbon mineralization in basalt fractures may yield a self-reinforcing feedback in which fracture intersections initially decrease flow rates by relative permeability effects, thus increasing fluid residence time and promoting mineral precipitation. These secondary alteration products decrease bulk fracture permeability, which reinforces the relative permeability feedback that decreases flow rates, increases fluid residence time and enhances mineralization. In the context of CCS, this feedback cycle suggests that basalt fracture networks may be self-sealing systems if CO₂ mobility approaches nil.

The present study employs reactive transport modeling to test the aforementioned mineralization-permeability feedback. We model free-phase CO₂ infiltration into a synthetic basalt fracture when permeability is coupled with porosity, both of which changes dynamically during simulation as mineral dissolution and precipitation alter pore volume in the fracture, i.e., porosity-permeability coupling. Results show that even small changes permeability (weak porosity-permeability coupling) dramatically increases CO₂ mineralization potential, while the stronger porosity-permeability coupling effectively seals the fracture network as fluids become immobile.

2. Methods

2.1. Conceptual model

Our conceptual model considers the effects CO₂ leakage within a layered basalt formation (Fig. 1). In this scenario, the injection zone comprises high-permeability upper and lower columnar structures that are juxtaposed below a low-permeability basalt flow entablature with fanning, tightly-welded fracture networks (Fig. 1) (Pollyea and Fairley, 2012; McGrail et al., 2012). As CO₂ accumulates in the target injection zone, buoyancy drives leakage into the entablature fracture network. This leakage process was initially investigated in a meter-scale outcrop study (Gierzynski and Pollyea, 2017), which showed that free-phase CO₂ accumulates at fracture intersections before diverging into branching fractures (Fig. 1). This phenomenon occurs because relative permeability effects decrease CO₂ mobility when a single flow path diverges into two or more branching fractures (Fig. 2). In basalt fractures, relative permeability is highly interfering (Bertels et al., 2001), thus small changes in non-wetting phase saturation cause significant changes in both wetting- and non-wetting phase permeability. As a consequence, CO₂ mobility in a fractured basalt is inhibited when a single flow path splits into one or more branching flow paths because the CO₂ saturation in each branch is substantially lower than in the main trunk (Fig. 2). The implication of this relative permeability effect is that fluid residence time may increase at branching fractures, thus encouraging carbon mineralization reactions. However, Gierzynski and Pollyea (2017) focused solely on non-reactive multi-phase flow processes, and feedbacks between fluid mobility, fluid-rock reactions, and permeability changes caused by mineral precipitation remain an open question.

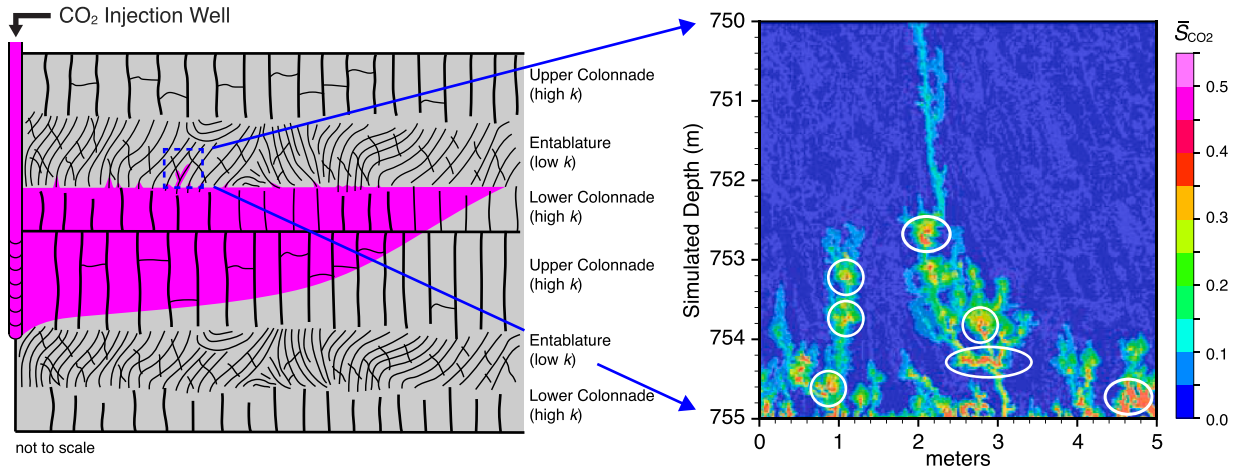


Figure 1. Left panel illustrates the conceptual model scenario in which (i) free-phase CO_2 is injected into the high-permeability zones (upper and lower colonnades) of layered basalt formation and (ii) buoyant CO_2 migrates upward into the low permeability entablature zone. Right panel presents ensemble simulation results showing that CO_2 saturation tends to accumulate at fracture intersections (white ellipses) due to relative permeability effects; image adapted from Gierzynski and Pollyea (2017).

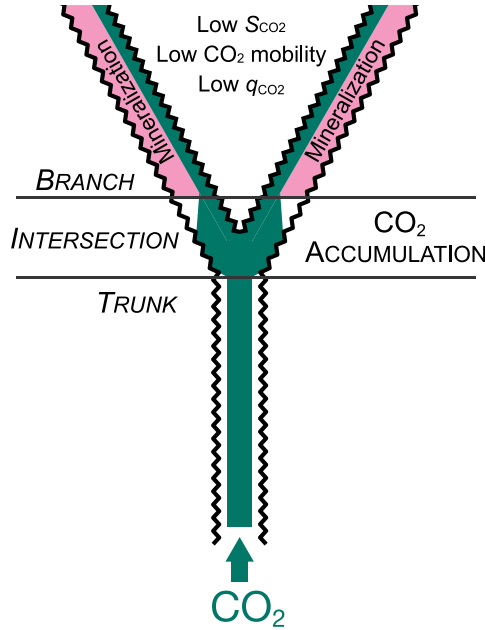


Figure 2. Conceptual schematic of free-phase (supercritical) CO_2 flow in a branching fracture. The CO_2 mobility will decrease as a conductive fracture (trunk) splits into two or more branching fractures.

These feedbacks are interrogated in the present study by simulating CO_2 infiltrating a synthetic fractured basalt in which a single fracture diverges into two branching fractures (Fig. 2). We implement reactive transport simulation to consider the competing effects of buoyancy (Wu et al., 2018, 2021) and permeability alteration that occurs as fracture porosity is reduced by precipitation of secondary mineral phases (Luhmann et al., 2017a). In doing so, we evaluate feedbacks between carbon mineralization, porosity-permeability coupling, and CO_2 mobility, particularly in the context of their relationship to CCS efficacy in basalt formations. In addition, we test four non-linear porosity-permeability coupling models with increasing coupling strength to evaluate the potential for a fracture network in basalt to self-seal.

2.2. Domain and boundary conditions

The model domain for this study is a 2-D synthetic basalt fracture system that rises 1.5 m from the base and branches at 45° (Fig. 3). The complete model domain is $2.5 \text{ m} \times 2.5 \text{ m}$ with 10,000 grid cells that are discretized $0.025 \text{ m} \times 0.025 \text{ m}$. The fracture domain is modeled as a porous media equivalent with permeability of $6 \times 10^{-16} \text{ m}^2$, which represents mean basalt fracture permeability at depths of $\sim 750 \text{ m}$ (Gierzynski and Pollyea, 2017; Jayne and Pollyea, 2018). The van

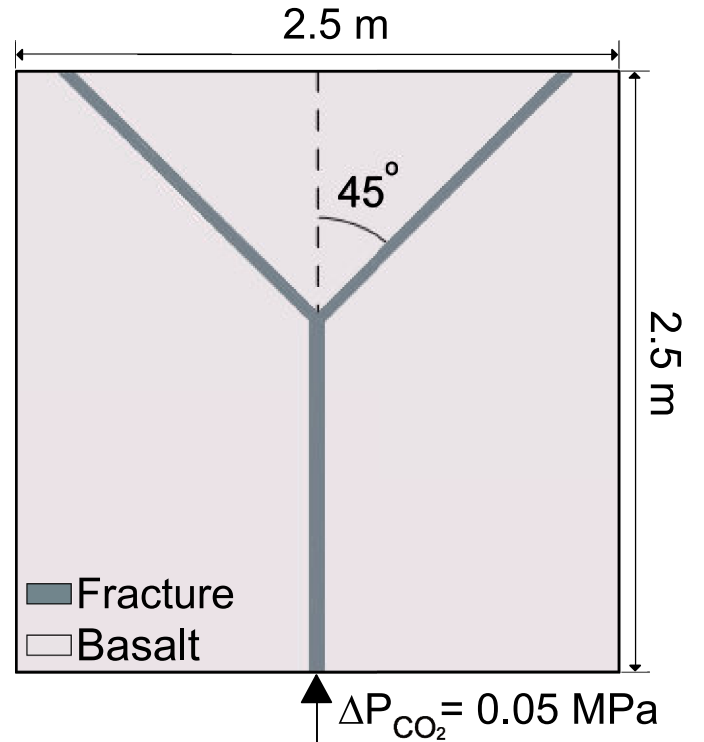


Figure 3. Conceptual schematic of the 2-D model domain implemented for this study. The domain is a $2.5 \text{ m} \times 2.5 \text{ m}$ area that is discretized into 10,000 grid cells with $0.025 \text{ m} \times 0.025 \text{ m}$ dimensions. The centrally located fracture (gray) splits into two diverging fractures at 1.5 m from the base. The basal boundary simulates CO_2 leakage from below with 0.05 MPa of overpressure. The upper boundary is specified as a Dirichlet condition.

Genuchten relative permeability model is parameterized to be highly interfering (Table 1), which is congruent with experimental results from (Bertels et al., 2001). Unfractured basalt (matrix) permeability is specified as 10^{-20} m^2 on the basis of literature values ranging between 10^{-17} and 10^{-24} m^2 (Bertels et al., 2001; Nara et al., 2011; Walker et al., 2013a,b).

The model scenario considers free-phase CO_2 migrating upwards from a disposal reservoir into the overlying basalt flow interior, i.e., reservoir leakage (Fig. 1). To facilitate this scenario, initial conditions are specified as 7.5 MPa and 33°C , which corresponds to a depth of $\sim 750 \text{ m}$, and free-phase CO_2 enters the fracture from below with 0.05 MPa of overpressure. Initial water composition is in thermodynamic equilibrium with basalt and salt concentration is 10,000 ppm. Lateral boundaries are adiabatic (no flux) and the top boundary is open (Dirichlet) to allow mass and heat flow into or out of the system. The remaining hydraulic and thermal properties are shown in Table 1. The code selection for this study is TOUGHREACT v3.2-OMP, complied with the equation of state module ECO2N, which simulates thermodynamic properties for various components of the system, as well as geochemical species transport, fluid-rock reactions and porosity change due to mineral dissolution and precipitation (Xu et al., 2014).

2.3. Reactive transport simulation

When free-phase CO_2 is injected into basalt reservoirs, the carbon mineralization process is characterized by a series of reactions. The first step is CO_2 dissolution into the aqueous phase, which yields hydrogen and bicarbonate ions,



This reaction releases H^+ ion into solution, which decreases pH and drives basalt dissolution. The whole-rock dissolution reaction for Icelandic basalt is given by Oelkers and Gislason (2001) and Gudbrandsson et al. (2011) as,

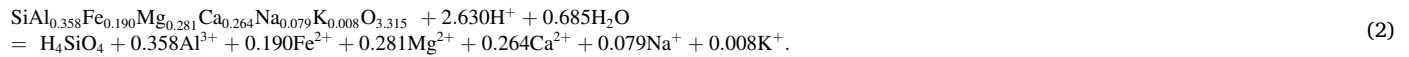
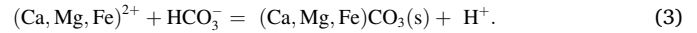


Table 1
Material properties used in this model

Rock and fluid properties			
Property	Symbol	Value	Units
Fluid Pressure	P_f	7.5	MPa
Temperature	T	33	$^\circ\text{C}$
Salinity	C_{NaCl}	10,000	ppm
Permeability (basalt)	k_b	10^{-20}	m^2
Permeability (fracture)	k_f	6×10^{-16}	m^2
Porosity (basalt)	ϕ_b	0.05	-
Porosity (fracture)	ϕ_f	0.10	-
Density	ρ_r	2950	kg m^{-3}
Specific heat	C_p	840	J (kg K)^{-1}
Thermal conductivity	κ_r	2.11	W (m K)^{-1}
Relative permeability model			
Property	Symbol	Value	Units
van Genuchten fitting parameter	λ	0.457	-
Residual liquid saturation	S_{lr}	0.3	-
Saturated liquid saturation	S_{ls}	1.0	-
Residual gas saturation	S_{gr}	0.25	-

This reaction consumes H^+ ion and releases divalent cations (Mg^{2+} ,

Ca^{2+} , Fe^{2+}) into solution, which then react with the available bicarbonate ion to produce carbonate minerals,



In addition to carbonate minerals, the Al and Si released during basalt dissolution react to form clay minerals (e.g., montmorillonite and illite). As secondary mineral alteration progresses, additional H^+ ion is released, which further drives basalt dissolution (Gysi and Stefánsson, 2012).

Cation release from basalt dissolution (Eq. 2) is generally considered the rate-limiting step in CO_2 mineralization (Oelkers et al., 2008). In this context, the rate of basalt dissolution is equivalent to the rate of silica release (J_{Si}),

$$J_{\text{Si}} = k a_{\text{H}^+}^n = (A e^{-1000 E_a / RT}) a_{\text{H}^+}^n \quad (4)$$

where k is the rate constant ($\text{mol m}^{-2} \text{ sec}^{-1}$), a_{H^+} is the hydrogen ion activity, n is the reaction order, A is the pre-exponential for the Arrhenius equation ($\text{mol m}^{-2} \text{ sec}^{-1}$), E_a is activation energy (kJ mol^{-1}), R is the gas constant ($\text{J mol}^{-1} \text{ K}^{-1}$), and T is the temperature (K). Equation 4 shows that the rate constant (k) is controlled largely by temperature and pH (Gudbrandsson et al., 2011). For Equation 2, this relationship was quantified by Pollyea and Rimstidt (2017), who developed rate equations for both crystalline and glassy basalt dissolution on the basis of experimental data compiled from the literature. These rate equations use the Palandri and Kharaka (2004) formulation, which considers the overall dissolution rate to be the sum of independent parallel reactions that are temperature- and pH-dependent. In this formulation, the rate constant (k in $\text{mol m}^{-2} \text{ s}^{-1}$) is given as,

$$k = k_{298}^{nu} \exp \left[\frac{-E_a^{nu}}{R} \left(\frac{1}{T} - \frac{1}{298.15} \right) \right] + k_{298}^H \exp \left[\frac{-E_a^H}{R} \left(\frac{1}{T} - \frac{1}{298.15} \right) \right] a_{\text{H}^+}^{n_H} + k_{298}^{OH} \exp \left[\frac{-E_a^{OH}}{R} \left(\frac{1}{T} - \frac{1}{298.15} \right) \right] a_{\text{OH}}^{n_{OH}} \quad (5)$$

Each term on the right side of Equation 5 represents a parallel reaction for near-neutral pH, low pH and high pH, which are denoted by superscripts *nu*, *H*, and *OH*, respectively. For each parallel reaction, k_{298} is the reaction rate at 298 K (25°C) ($\text{mol m}^{-2} \text{ s}^{-1}$), E_a is activation energy (J mol^{-1}), T is temperature (K), R is the gas constant ($8.314 \text{ J mol}^{-1} \text{ K}^{-1}$), a_{H} (or a_{OH}) is the activity of hydrogen (or hydroxide), and n_{H} (or n_{OH}) is the reaction order for hydrogen (or hydroxide). Pollyea and Rimstidt (2017) fit the linearized version of Equation 4 to whole-rock basalt dissolution data from the literature (Gudbrandsson et al., 2011) and found that the rate of basalt dissolution (Eq. 2) reaches a minimum at pH 6 without an apparent near-neutral rate plateau, thus the first term on the right side of Equation 5 goes to zero. The remaining terms in Equation 5 were parameterized by Pollyea and Rimstidt (2017) for modeling whole-rock basalt dissolution (Table 2); the resulting rate

Table 2
Kinetic rate equation parameters for whole-rock basalt dissolution

	$\log k_{25}$	E_a	n	R
pH < 6	-6.15	40.1	-0.680	8.314 (J/mol K)
pH > 6	-11.83	32.9	0.286	8.314 (J/mol K)

^a k is the rate constant ($\text{mol m}^{-2} \text{ sec}^{-1}$), subscript 25 denotes the reaction rate at 298 K (25°C), E_a is activation energy (kJ mol^{-1}), n is the reaction order, and R is the gas constant ($\text{J mol}^{-1} \text{ K}^{-1}$).

Table 3
Geologic materials simulated in this model

Material	Mode for Geochemical Reaction [†]
Basalt [‡]	Dissolution
Calcite	Precipitation
Magnesite	Precipitation
Siderite	Precipitation
Montmorillonite (MgCa)	Precipitation
Illite(FeII)	Precipitation
Amorphous silica	Precipitation

[†] Dissolution by kinetic constrains (Eq. 4). Precipitation by local equilibrium.
[‡] Whole-rock basalt dissolution (Eq. 2) using the rate equation developed by Pollyea and Rimstidt (2017).

equation is valid for the pH and temperature ranges, $2 < \text{pH} < 12$ and $0^\circ\text{C} < T < 100^\circ\text{C}$.

The second step for CO_2 mineralization is mineral precipitation. The alteration products for this study include carbonate phases (calcite, magnesite, siderite), clay minerals (montmorillonite, illite), and amorphous silica (Table 3). Because basalt dissolution is generally considered to be the limiting step in carbon mineralization, we model the precipitation of these secondary alteration products on the basis of local equilibrium. The thermodynamic database utilized for these reactions is based on Thermodem v.1.10 (Blanc et al., 2012) and modified by Pollyea and Rimstidt (2017) to include solubility constants for whole-rock basalt dissolution. Complete description of the precipitation reactions is included as Electronic Supplementary Material.

2.4. Permeability alteration

Dissolution and precipitation reactions alter the pore space of the fracture network, which in turn affects porosity and permeability. Among the principal questions in basalt sequestration is how permeability is affected by the precipitation of secondary mineral phases. For a

parallel-plate fracture, uniformly distributed mineral precipitation along the fracture walls decreases permeability (k) as the product of initial permeability (k_i) and the cube of the ratio of time-varying porosity (ϕ) to initial porosity (ϕ_i),

$$k = k_i \left(\frac{\phi}{\phi_i} \right)^3. \quad (6)$$

This porosity-permeability relationship is commonly known as the *cubic law* (Fig. 4A); however, Schaef et al. (2011) found calcite precipitation in the CO_2 -water-basalt experiments forms a variety of discrete round nodules that suggests uniform scaling of the fracture wall is unlikely (Fig. 4B). This result was corroborated by examination of post-injection sidewall cores from the Wallula Basalt Sequestration Pilot Project, which showed that discrete carbonate nodules were widespread throughout the injection zone. Similarly, Xiong et al. (2017b) discovered that carbonate minerals are distributed unevenly along a basalt fracture, including the occurrence of carbonate bridges that span across the fracture aperture (Fig. 4C). These results all suggest that the parallel-plate cubic law may underestimate the degree to which permeability is affected by carbon mineralization. For example, the formation of nodules protruding from the fracture wall may cause substantially lower fracture permeability for relatively small changes in porosity. And, for the extreme case in which alteration products form a discrete bridge across a fracture, the permeability may approach nil, thus sealing the fracture even though the change in porosity is very small (Fig. 4C). To account for these phenomena, we invoke a modification of the Verma and Pruess (1988) porosity-permeability model that frees the exponent of the cubic law to facilitate variable porosity-permeability coupling,

$$k = k_i \left(\frac{\phi}{\phi_i} \right)^n. \quad (7)$$

Here, we refer to equation 7 as the “power-law dependent permeability” (PLDP) equation in which the relationship between the porosity change resulting from mineralization and its effect on permeability

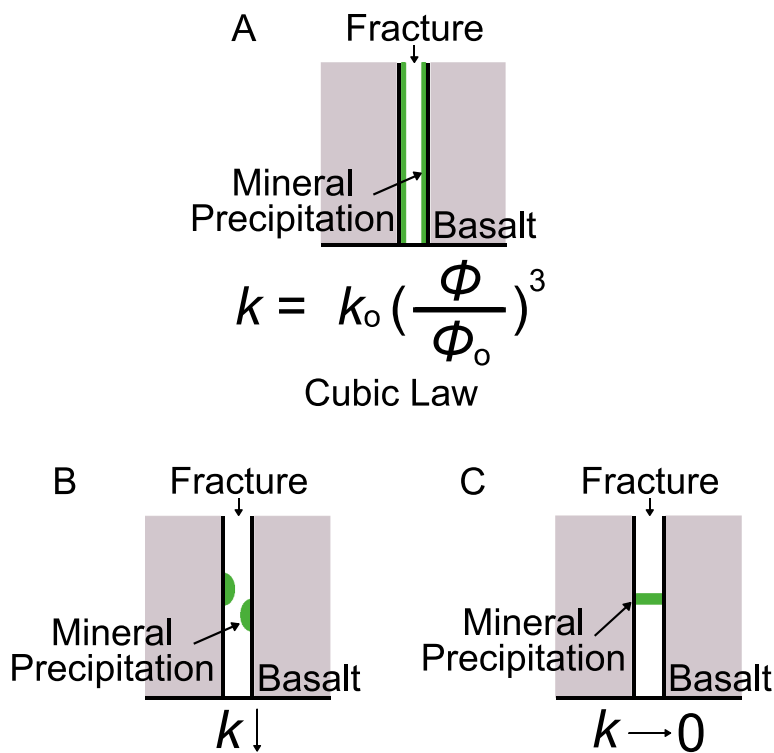


Figure 4. Conceptual schematic of different mineralization patterns within a fracture system. Panel A presents uniformly distributed mineralization on a parallel-plate fracture, the result of which is quantified by the cubic law ($n = 3$ in Equation 7). Panels B and C illustrate mineralization occurring as nodules and as a bridge that spans the fracture aperture, respectively, which reflect stronger ϕ - k coupling ($n > 3$ in Equation 7), i.e., large permeability reduction with small porosity change.

depends on the geometrical characteristics of the precipitating material, i.e., planar deposition along the walls of the fracture, nodular deposits, bridges across fracture apertures, etc. These geometrical characteristics are reflected in the value of the *strength of coupling* exponent, n . For this study, we simulate reactive CO₂ flow for five individual simulations such that the strength of coupling exponent n in Equation 7 is 0, 3, 6, 9, and 15. The case where n equals 0 corresponds to the condition in which porosity-permeability coupling is absent; the case for $n = 3$ is the well-known cubic law; and the cases for n equals 6, 9, and 15 represent systematically stronger porosity-permeability couplings. That is, as the

magnitude of the exponent increases, the permeability is affected to an increasingly greater extent by the change in porosity. As a result, the simulations consider permeability to be a dependent variable that changes dynamically based on the difference between the volume of basalt that dissolves and the volume of secondary minerals that precipitate. These volumes, in turn, are calculated based on the molar proportions of minerals dissolving and precipitating and the molar volumes of those minerals.

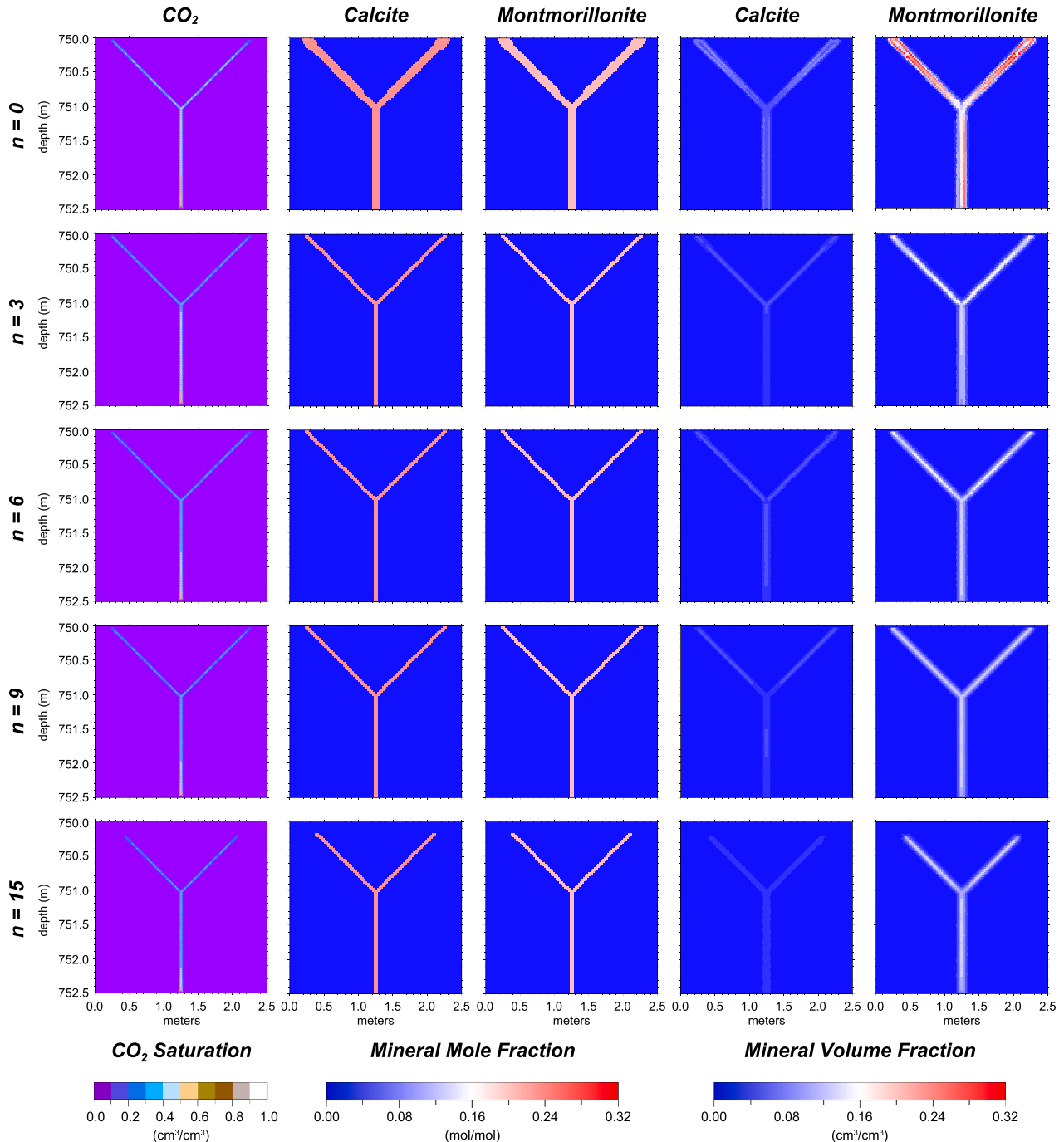


Figure 5. Simulation results after 10 years of CO₂ leakage at 0.05 MPa overpressure. Left column shows CO₂ saturation; remaining columns show molar and volume fractions for calcite and montmorillonite. Mole fraction is calculated as the ratio of moles of mineral to total moles of all secondary minerals. Volume fraction is calculated as the ratio of the volume of the mineral to the initial pore volume. Rows correspond to calculations involving equal strength of porosity-permeability coupling as described by the exponent n in Equation 7.

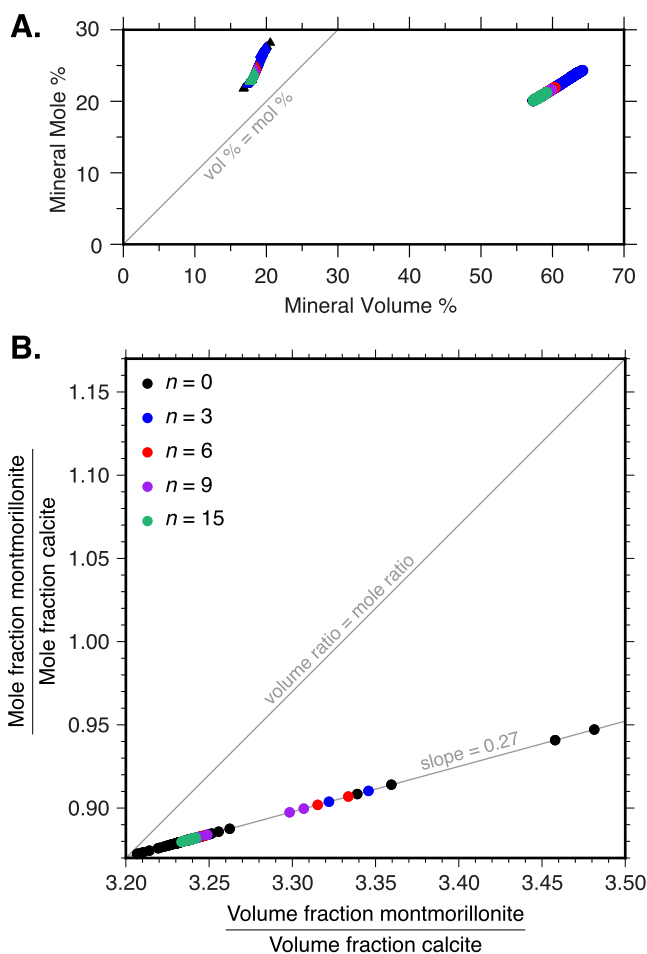


Figure 6. Comparison of molar and volume abundances for calcite and montmorillonite. Panel A compares mineral mole percent and mineral volume percent for calcite (triangles) and montmorillonite (circles). For each grid cell, mole percent is calculated as the moles of calcite (or montmorillonite) divided by the total moles of all secondary minerals that form in the grid cell. Volume percent is calculated as the volume of calcite (or montmorillonite) divided by the total volume of all secondary minerals. As shown, the mole percent of calcite formed always exceeds its volume percent in the pore space. Panel B compares the mole fraction ratio of montmorillonite-to-calcite with the volume fraction ratio of montmorillonite-to-calcite for each PLDP scenario (i.e., n in Equation 7). These data collapse to a single line with slope of 0.27 because the molar volume of calcite is $0.27 \times$ the molar volume of montmorillonite. Stated differently if equi-molar proportions of calcite and montmorillonite precipitate in the pore space, the volume of the calcite formed will be $0.27 \times$ the volume of montmorillonite formed.

3. Results and discussion

In the discussion that follows, simulation results are presented with respect to the strength of coupling exponent, n , in the porosity-permeability (ϕ - k) coupling relationship described by Equation 7. Figure 5 presents the results of CO_2 saturation and secondary mineral abundance after 10 years of simulation. Mineral abundance is calculated for each grid cell in terms of both mole fraction and volume fraction. In Figure 5, volume fraction is the ratio of the volume of a given mineral (calcite, montmorillonite) to initial pore space volume, while mole fraction is the ratio of moles of a mineral (calcite, montmorillonite) to the total moles of all secondary minerals precipitated. The mineral abundance calculations are compared in Figure 6 for both calcite and montmorillonite to emphasize the significant differences between volume proportions and molar proportions of secondary

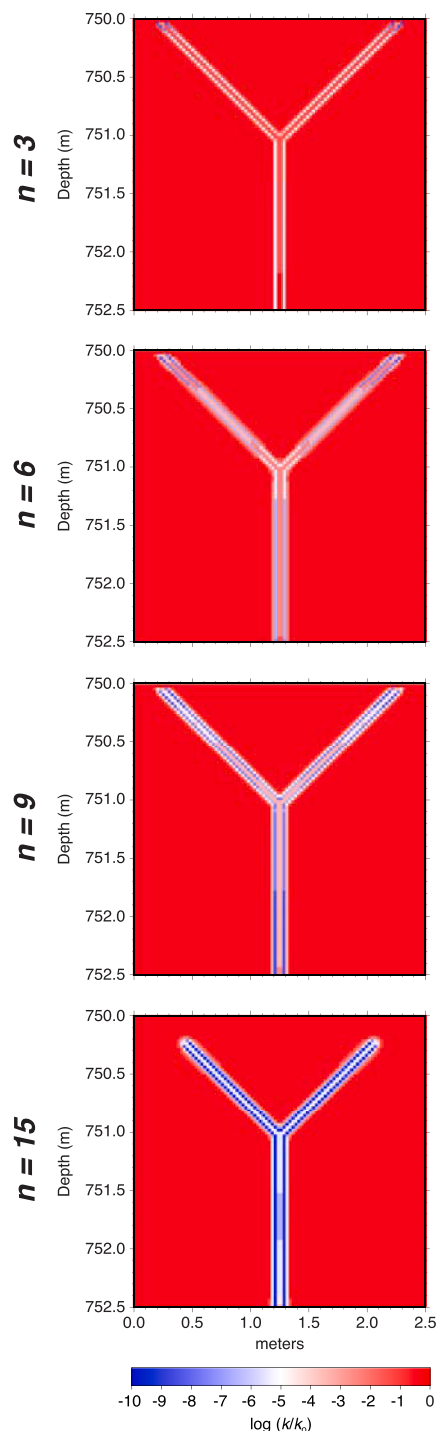


Figure 7. Change in permeability within the fracture for each porosity-permeability model after 10 years of CO_2 leakage at 0.05 MPa overpressure. For each panel, n corresponds with the strength-of-coupling exponent in Equation 7.

minerals formed. Mineral abundances for the remaining secondary minerals are illustrated in Electronic Supplementary Material as Figure S1 and Figure S2, respectively. Figure 8 illustrates the permeability change in the fracture as a result of CO_2 -water-basalt reactions after 10 years. The temporal change of free-phase CO_2 mobility is presented as Darcy flux in Figure 8 for different positions within the fracture, and the corresponding temporal change in permeability is shown in Figure 9.

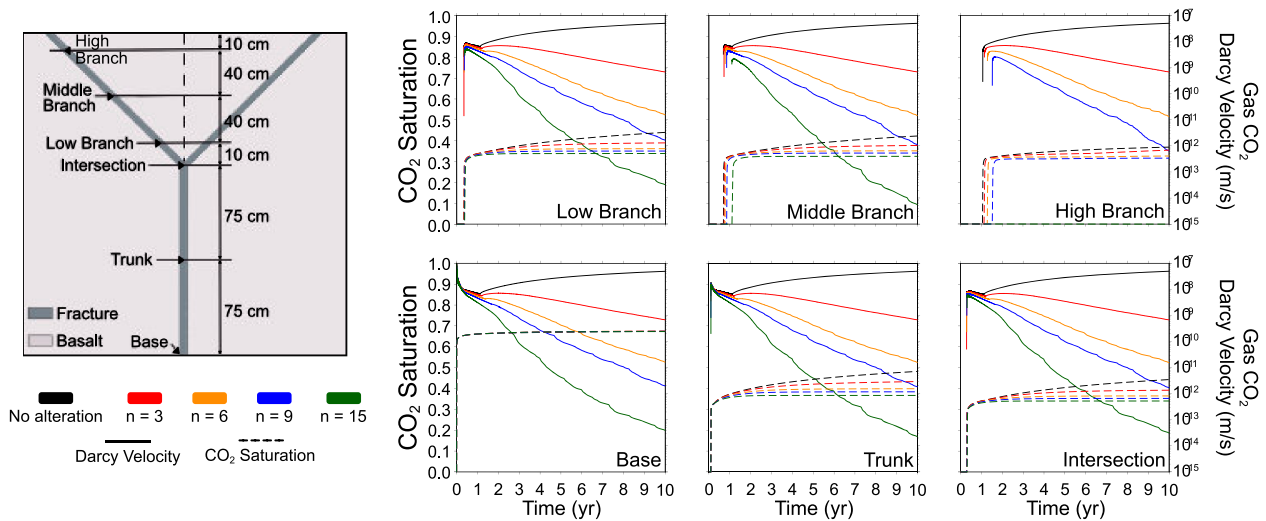


Figure 8. Left figure presents the six reference locations along the fracture. Right figure presents the CO₂ saturation and CO₂ phase Darcy velocity at different positions with different porosity-permeability strength of coupling exponents, n .

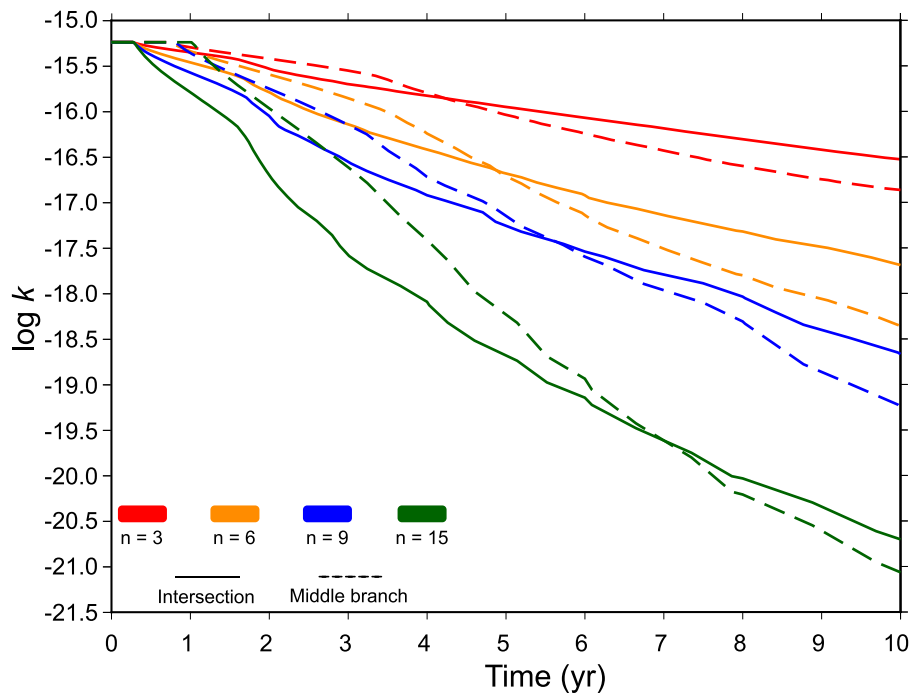


Figure 9. Time series of fracture permeability change at the fracture intersection and middle branch with different porosity-permeability strength of coupling exponents, n .

3.1. Mineral precipitation and fracture permeability evolution

Results from this study show that secondary mineral precipitation is widespread in each simulation. As noted above, we plot both the volume proportions and molar proportions of the secondary minerals calcite and montmorillonite in Figure 5. The reason for doing so is that the volume fractions reflect the relative role of each mineral phase in affecting fluid flow, whereas the molar fractions reflect the geochemical environment related to the extent of CO₂-water-basalt reactions. Calcite is the most abundant secondary mineral on a mole fraction basis (Fig. 5) with appreciable amounts of magnesite and siderite also formed (Fig. S2). These results are generally consistent with Matter et al. (2016), who report that calcite was the most abundant alteration product during carbon mineralization at the CarbFix pilot project in Iceland. Due to the

large molar volume of montmorillonite (compared to calcite and other simple carbonate minerals described here), our results suggest that clay minerals comprise a significant volume fraction of mineralization in the pore space despite its lower molar abundance compared to calcite (Fig. 5). This relationship is further explored in Figure 6A, which shows that the mole percent (mol%) calcite exceeds its corresponding volume percent (vol%) within the fracture, while mol% montmorillonite is substantially lower than its corresponding vol%. By comparing the ratio of mole fraction montmorillonite to mole fraction calcite with the ratio of volume fraction montmorillonite to volume fraction calcite (Fig. 6B), we also find that the data for all PLDP scenarios collapse onto a single line with slope of ~ 0.27 . This phenomenon reflects the fact that the molar abundance of calcite in the fracture is only slightly greater than the molar abundance of montmorillonite (Fig. 5); however, the molar

volume of calcite is $37 \text{ cm}^3/\text{mol}$, while the molar volume of montmorillonite is $136 \text{ cm}^3/\text{mol}$, i.e., the molar volume of calcite is $0.27 \times$ the molar volume of montmorillonite.

Simulation results for each model scenario show that free-phase CO_2 saturation (defined as the proportion of available pore space occupied by the CO_2 phase) reaches ~ 0.8 at the fracture base but then varies substantially in the fracture branches depending on the strength of the ϕ - k coupling. In particular, the scenario without ϕ - k coupling ($n = 0$ in Eqn. 7) shows that CO_2 saturation in the fracture branches reaches ~ 0.4 after 10 years (Fig. 5, upper left panel). In contrast, the cases that dynamically alter permeability as a function of porosity (Eq. 7) show that CO_2 saturation decreases as the strength of porosity-permeability coupling increases. We also find that all CO_2 remains in the fracture after 10 years of leakage for the case in which n equals 15 (Fig. 5, lower left panel). In general, these behaviors demonstrate that vertical CO_2 migration is highly sensitive to the strength of coupling in the porosity-permeability relationship defined by equation 7. These results also illustrate that both CO_2 saturation in the fracture as well as the secondary mineral molar and volume abundances both vary inversely with the strength of the ϕ - k coupling. For example, the model scenario lacking porosity-permeability coupling ($n = 0$ in Equation 7) results in the highest molar and volume abundances of secondary alteration products (Fig. 5, Fig. S2). This occurs because CO_2 migrates more rapidly through unaltered flow path, such that the basalt is exposed to the CO_2 -water mixture for a longer time period, thus increasing the time that CO_2 mineralization reactions (Equations 1 – 3) can proceed. As the ϕ - k coupling becomes stronger (i.e., as n increases), the abundance of secondary minerals systematically decreases because the CO_2 flow rates decrease, thus decreasing the time that basalt is exposed to the CO_2 -water mixture. This interpretation is congruent with laboratory studies that show basalt dissolution as the rate-limiting step in CO_2 mineralization (Matter and Kelemen, 2009).

In the context of fracture geometry, mineralization after 10 years of simulation is generally widespread throughout the fracture but tends to accumulate in greater abundance within the fracture branches for all ϕ - k coupling scenarios. Here, we use the term “abundance” to refer to the number of moles of mineral precipitated, which is proportional to the volume of mineral precipitated. For example, the largest amount of calcite precipitation occurs for the $n=0$ case; however, it is also apparent that calcite is abundant within matrix grid cells that are adjacent to the fracture. When PLDP is simulated, calcite abundance decreases as the strength of the porosity-permeability coupling increases (Fig. 5), i.e., as the magnitude of the exponent n in equation 7 increases. These results generally support the hypothesis that mineral precipitation is highest downgradient from fracture intersections. To evaluate the degree to which mineralization affects fracture permeability, Figure 7 illustrates the change in bulk fracture permeability as a function of the strength of the ϕ - k coupling. Note that the scenario for $n=0$ is not shown in Figure 7 because there is no porosity-permeability coupling. For the parallel-plate ($n=3$) scenario, permeability decreases by a factor of $\sim 1 \times 10^{-5}$ along the fracture walls; however, the conductive portion of the fracture maintains its original permeability. This PLDP pattern matches the mineralization patterns illustrated in Figure 5. As the strength of ϕ - k coupling increases, permeability is reduced substantially. For the case where $n=15$, permeability approaches nil, decreasing by a factor of $\sim 1 \times 10^{-10}$, along the fracture walls and by a factor $\sim 1 \times 10^{-6}$ in conductive portions of the fracture. Interestingly, these results also show that the effect of strength of coupling is generally smaller at fracture intersections for all cases involving PLDP, i.e., when $n > 0$. This phenomenon may occur because relative permeability effects decrease mobility of both wetting and non-wetting phase fluids at the intersection, which inhibits mineralization as the trapped fluids approach equilibrium with the basalt and the bicarbonate ion is consumed.

The results presented in Figure 7 illustrate that permeability reductions are most pronounced along the wall of the fracture, regardless of the PLDP equation exponent. Stockmann et al. (2008) developed

batch experiments of diopside dissolution and observed that calcite precipitated at the diopside surface. Additionally, experimental results indicate that precipitation of secondary minerals on the surface reduces the reactive surface area and decreases the dissolution rate (Hövelmann et al., 2012; Andreani et al., 2009). However, in the context of CCS these results imply that the rate of CO_2 mineralization may decrease with time because the dissolution rate of basalt decreases with time as mineral precipitation occurs along the fracture wall. This effect decreases the reactive surface area, which results in fewer divalent cations (Ca^{2+} , Mg^{2+} , Fe^{2+}) in the solution to promote mineral precipitation (Wells et al., 2017). However, the volume of the secondary minerals is greater than that of the basalt that is being dissolved, which may generate stresses that exceed the tensile strength of the host rock thus creating new (unaltered) surface area for reactions to occur.

While the results for model scenarios with ϕ - k coupling strength of $n=3, 6$, and 9 show similar PLDP patterns, the model scenario with $n=15$ is unique because the PLDP pattern is uniform throughout the fracture system (Fig. 7). This phenomenon occurs because permeability decreases substantially as alteration minerals begin to form. As a consequence, CO_2 mobility decreases dramatically, and the PLDP pattern appears to migrate contemporaneously with CO_2 migration through the fracture, as is evident by comparing the PLDP pattern in Figure 7 (bottom panel) with the CO_2 saturation pattern in Figure 5 (bottom left). Moreover, these results show that there is no CO_2 leakage out of the system through the upper boundary after 10 years of simulation, which suggests that strong ϕ - k coupling may generate a self-sealing fracture network; however, additional research is needed to learn (i) how mineral bridging affects fracture propagation and (ii) how mineral precipitation patterns develop in natural basalt fracture networks with 3-D geometry.

3.2. Spatial and temporal evolution in fracture permeability

In order to evaluate the relationship between CO_2 mobility and strength of porosity-permeability coupling in the basalt-water- CO_2 system, Figure 8 presents a time-series of CO_2 saturation and Darcy flux for six positions within the fracture. For discussion, these locations are referred to as base, trunk, intersection, low, middle, and high branch as defined within Figure 8. The base location is the bottom of the fracture, where CO_2 enters into the system, so time series results from this location can be interpreted as the leakage signal into the fracture network from the underlying reservoir.

From a temporal perspective, the overall pattern is that CO_2 mobility (as measured by Darcy flux) decreases systematically over time for all model scenarios that account for variable ϕ - k coupling; however, the CO_2 mobility increases over time for the model without ϕ - k coupling ($n=0$; Fig. 8). For this latter model scenario ($n=0$), the phenomenon in which CO_2 mobility initially decreases and then increases through time (Fig. 8, black curves) is related to relative permeability effects. When CO_2 initially enters the fracture, the relative permeability available to CO_2 is low because CO_2 saturation is low and fractures in basalt are known to exhibit highly interfering relative permeability behavior (Bertels et al., 2001). This causes the CO_2 mobility to remain low; however, relative permeability increases over time as more CO_2 enters the fracture, the result of which increases CO_2 mobility over time. This phenomenon is also apparent for the cubic ϕ - k coupling scenario ($n = 3$) within the first 2.5 years (Fig. 8, red curve); however, after 2.5 years, the Darcy flux steadily decreases because permeability loss as a result of mineralization overwhelms the relative permeability effects. For stronger ϕ - k coupling ($n \geq 6$), CO_2 mobility at each location in the fracture decreases systematically with time as mineralization fills pore space. For the strongest ϕ - k coupling scenario ($n=15$), CO_2 flux decreases by six orders of magnitude after 10-years, thus effectively sealing the fracture because free-phase CO_2 never reaches the high-branch monitoring location.

The spatial variation of CO₂ mobility within the fracture network shows little variation within each scenario, except for the strongest ϕ - k coupling ($n = 15$). This result is congruent with the well-known phenomenon that fluid flow rates in fractures are controlled by the smallest openings available for flow. The sole exception to this pattern is the $n = 15$ scenario, which shows up to an order of magnitude variation in CO₂ mobility along the flow path. For this scenario, CO₂ mobility decreases systematically in the direction of flow and goes to nil at the high branch monitoring location because CO₂ has not reached this location after 10 years. This reduction in flow rate occurs because of mineral precipitation, which is most pronounced in the middle branch regions of the fracture system and effectively shuts off CO₂ flow to the high-branch portions of the fracture network.

For this study, decreasing CO₂ mobility is driven primarily by changes in permeability associated with mineralization in the fracture. The temporal change in permeability for each ϕ - k coupling scenario is shown in Figure 9 at the fracture intersection and middle branch. The PLDP variations range from ~ 2 orders of magnitude for the parallel-plate ($n=3$) model to more than 5 orders of magnitude for the $n=15$ scenario. For each of these model scenarios, permeability reduction occurs first at the fracture intersection because this location experiences the first exposure to CO₂ (Fig. 9, solid lines). However, once mineralization occurs in the middle branch, permeability changes occur at a faster rate, and within 10 years, the overall permeability loss in the middle branch exceeds permeability losses at the intersection, for all model scenarios. This tendency for permeability changes to be most pronounced in the middle branch occurs because the CO₂ mass is halved when flowing into the fracture branches from the main trunk. As a consequence, the relative permeability is lower in the branches, which slows the mobility of both free-phase CO₂ and the aqueous phase. This increases residence time for the aqueous phase and promotes basalt alteration in the fracture branch. These relative permeability effects also cause CO₂ to accumulate at the fracture intersection, which inhibits fluid-rock interaction.

3.3. Carbon balance & mineralization

Geologic CO₂ sequestration in basalt formations is predicated on rapid CO₂ mineralization following injection (McGrail et al., 2006). At the CarbFix site in Iceland, pilot-scale injections of aqueous phase CO₂ found that more than 95 mass % of the injected carbon was mineralized in less than two years (Matter et al., 2016). These results were based on mass balance calculations between dissolved organic carbon and ¹⁴C tracers, which found substantial reductions in both along the flow path of the target reservoir. For this to occur, the most plausible mechanism is the formation of carbonate minerals. Although similar testing was not performed at the Wallula site in Washington State, USA, where free-phase CO₂ was injected at ~ 750 m depth, analysis of post-injection sidewall cores from the borehole found that carbonate minerals (primarily ankerite) were widespread (McGrail et al., 2017). More recently, White et al. (2020) found that carbonate minerals filled

$\sim 4\%$ of the original pore volume when inspecting post-injection sidewall cores from the Wallula project.

To assess the relationship between mineralization-induced permeability variations, mineralization potential, and storage efficacy, we balance the moles of carbon entering the fracture and the subsequent molar abundance of carbon among solid, aqueous, and CO₂ fluid phases for each ϕ - k coupling scenario after 10 years of simulation (Table 4). For the CO₂ leakage scenario simulated here, there is no carbon in the system prior to CO₂ infiltration, thus balancing the carbon provides a straightforward assessment of the carbon mineralization potential as a function of the strength of ϕ - k coupling, i.e., the magnitude of the exponent, n , in equation 7. For this model scenario, free-phase CO₂ enters the fracture from below, and, as it rises, may dissolve in the aqueous phase to produce various aqueous CO₂ species (i.e., CO₂ dissolved in water) and/or precipitate carbonate minerals such as calcite, magnesite, and siderite. In addition, CO₂ may exit the analytical volume through the upper boundary; however, the TOUGHREACT code treats Dirichlet boundaries as grid cells with semi-infinite volume. As a result, the total carbon mass in the upper boundary cells represent CO₂ leakage out of the fracture.

For each ϕ - k coupling scenario, we calculate the carbon mineralization ratio as the ratio of moles of carbon transformed into carbonate minerals to the total moles of carbon that entered the fracture as free-phase CO₂ fluid over the 10-year simulation (Table 4). These calculations reveal two distinct patterns. First, the model scenario with no coupling ($n = 0$) comprises a mineralization ratio of 57% after 10 years of CO₂ flow into the fracture. In contrast, the model scenarios that account for various extents of porosity-permeability coupling mineralize 81% to 92% of carbon introduced into the fracture, which is generally congruent with the 95% mineralization rate reported for the CarbFix project (Matter et al., 2016). The discrepancy is likely a result of the models considering free-phase CO₂, which is buoyant in comparison to formation fluids; whereas, aqueous phase CO₂ injections at CarbFix result in a higher density fluid that will tend to sink. For the model scenarios that simulate PLDP, stronger ϕ - k coupling leads to (i) systematically higher mineralization ratios and (ii) systematically lower CO₂ mass entering the system. The reason that higher ϕ - k strength of coupling leads to lower CO₂ entering the fracture is because the model is based on a hypothetical scenario in which a free-phase CO₂ plume is juxtaposed below a low-permeability basalt flow interior with 0.05 MPa overpressure. For a fixed overpressure, the rate of CO₂ flow entering the fracture is a function of permeability, and the rate of permeability reduction increases as the strength of ϕ - k coupling increases and permits less CO₂ to enter the overlying entablature (confining unit).

Perhaps the most significant result of this study is that the model scenario without porosity-permeability coupling ($n = 0$) results in ~ 3 times more CO₂ infiltration than the model scenarios that account for increasing strength of porosity-permeability coupling ($3 \leq n \leq 15$), the latter of which vary by only $\sim 26\%$ (Table 4). This broad disparity demonstrates that the extent of porosity-permeability coupling plays a fundamental role in calculations to estimate the potential for CO₂ storage and leakage in mafic reservoirs. Since empirical models of PLDP in natural fracture networks remain elusive, the general ϕ - k coupling model implemented for this study (Verma & Pruess, 1988) demonstrates that errors in the ϕ - k coupling model are likely to be much lower than errors introduced by omitting the effect of mineralization on permeability.

5. Conclusion

Geologic carbon storage in basalt reservoirs offers the potential to expand the geographic footprint of carbon capture and sequestration technology. Although recent basalt CCS projects in Iceland and Washington State, USA have shown rapid mineralization at field scales, substantial uncertainty remains concerning the dynamics of carbon mineralization at the scale of an individual fracture. Recent research

Table 4

CO₂ phase distribution and carbon mineralization ratio for each porosity-permeability coupling scenario

	$n = 0$	$n = 3$	$n = 6$	$n = 9$	$n = 15$
	C (mole)	C (mole)	C (mole)	C (mole)	C (mole)
Mineral	62.5	30.5	31.6	31.8	27.2
Aqueous	4.5	2.0	2.2	2.2	2.1
Gas	1.5	0.5	0.4	0.4	0.4
Boundary [†]	40.9	4.6	1.2	0.4	-
Total	109.4	37.6	35.4	34.8	29.7
Mineralization Ratio	57%	81%	89%	91%	92%

n is the power law exponent in Equation 7.

[†] Sum of liquid and aqueous phase carbon (as CO₂) that passed through the model domain into the upper boundary (leakage).

shows that relative permeability effects may cause free-phase CO₂ to accumulate at fracture intersections (Gierzynski & Pollyea, 2017); however, the relationship between this phenomenon and CO₂ mineralization has yet to be explored. The current study tests the hypotheses that: (1) secondary mineral precipitation is best developed in the branching fracture and (2) such mineralization decreases permeability in a manner that may result in a self-sealing fracture network. These hypotheses are tested using reactive transport simulation of CO₂ infiltrating a meter-scale, synthetic fracture system in basalt from below. This model scenario (Fig. 1) represents upward CO₂ migration from high-permeability target formation into an overlying low-permeability zone (i.e., basalt flow entablature). Permeability is coupled to porosity, and porosity varies dynamically as a function of changes in the volume of the pores due to dissolution and precipitation. Conclusions from this study are summarized as:

- 1 Carbonate and clay minerals are mostly precipitated in the branching fractures, where mass transfer in the fluid is dominated by diffusion. Stronger porosity-permeability coupling results in lower CO₂ mass entering the fracture and, thus, less mineral precipitation.
- 2 Vertical gas-phase CO₂ migration is inhibited by mineral precipitation, which causes fracture permeability to decrease. When modeling CO₂ storage in a basalt reservoir, the effects of mineralization (amount and style) are critically important for estimating the CO₂ mass that is sequestered and that which has leaked from the reservoir.
- 3 For strong ϕ - k coupling, i.e., high values of the exponent n in equation 7, the large carbon mineralization ratio suggests that the fracture system may be self-sealing due to secondary mineral precipitation; however, this result is based 2-D fracture geometry and additional research is needed to assess this phenomenon in natural environments.
- 4 Errors in the different ϕ - k coupling models are comparatively small in comparison to errors introduced by neglecting the effect of mineralization on permeability.

In aggregate, these results provide important insights into physical and chemical feedback mechanisms that govern CO₂ mineral trapping in basalt reservoirs. Specifically, this study improves our understanding of mineral precipitation within basalt fractures at field scales, while illustrating its effect on permeability change and CO₂ migration. Translating these results into successful, industrial-scale basalt CCS project requires (1) substantial advances in our ability to characterize basalt fracture networks in nature, (2) deeper understanding of mineral nucleation and growth processes, and (3) further research aimed at understanding the relationship between mineralization patterns, volume increases during crystallization and fracture initiation (Laubach et al., 2019), the latter of which may adversely affect CO₂ trapping potential in basalt formations (Zhu et al., 2016) or generate new surface area to promote carbon mineralization reactions. Nevertheless, this study clearly demonstrates that mineralization and its effects on permeability must be considered when modeling the CO₂ sequestration in basalt reservoirs.

CRediT authorship contribution statement

Hao Wu: Conceptualization, Methodology, Software, Validation, Formal analysis, Investigation, Resources, Data curation, Writing - original draft, Writing - review & editing, Visualization, Supervision, Project administration. **Richard S. Jayne:** Conceptualization. **Robert J. Bodnar:** Conceptualization. **Ryan M. Pollyea:** Conceptualization, Resources, Software, Formal analysis.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Supplementary materials

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