Permeability Evolution of a Cemented Volcanic Ash During Carbonation and CO$_2$ Depressurization

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Abstract The presence of calcium-cemented ash beds serving as caprocks in hydrothermal systems calls for the examination of any chemo-mechanical processes that may undermine or enhance their sealing capacity. Understanding these processes provides new information regarding how to model time-dependent observations associated with seismicity and/or deformation in volcanic areas. In addition, since these ash beds are inherently similar to ash-based concrete, a bridge of knowledge can be built across disciplines in the earth sciences and engineering. This paper investigates how the permeability of a volcanic ash cemented with hydrated lime changes upon exposure to carbon dioxide (CO$_2$) in humid and hydrous conditions relevant to natural or human-driven processes such as those found in hydrothermal settings or near wellbores used for secondary oil recovery, CO$_2$ plume geothermal energy, or carbon storage. We characterized samples by their permeability during carbonation and subsequent changes in pore pressure and confining pressure. Products from the reaction of CO$_2$ with the cemented ash matrix reduced permeability and entrapped fluids. The regions within samples permeated with unreacted CO$_2$ were susceptible to fracturing upon rapid depressurization, but only when the effective stress state was sufficiently low. Altogether, the results indicate that lime-cemented volcanic ash beds are particularly suited to act as flow barriers to CO$_2$-rich fluids.

Plain Language Summary This paper examines some of the physical characteristics of materials that are comprised of volcanic sediments and cemented together by a lime-rich fluid. Such materials can be described as either concrete-like rocks or rock-like concretes; thus, they are of interest to geophysical and engineering communities (and their hybrids), especially in regard to natural or human-made barriers for gases and fluids. A notable example of a gas that can be, or is desired to be, contained underground by rock formations and/or cemented structures is carbon dioxide (CO$_2$). However, it is important to realize that some of the most relevant properties of a rock or concrete serving as a barrier may actually be evolving during exposure to CO$_2$. Consequently, there is a need to understand the processes involved if we are to accurately predict the long-term efficacy of these seals. We injected CO$_2$ into samples of cemented volcanic ash and subsequently monitored the changes in their permeability while they chemically reacted. Our observations indicate that this particular material, when located at sufficient depth in the subsurface, can serve as a barrier to CO$_2$-rich fluid flow.

1. Introduction

Geologic materials are exposed to high concentrations of carbon dioxide (CO$_2$) in a variety of humid or hydrous subsurface environments. The production of CO$_2$ occurs naturally via the degassing of magma (Lowenstern, 2001), decarbonation of limestone and other rocks (Bickle, 1996), and maturation of organic matter (Abelson, 1978). CO$_2$ also enters formations by the injection through wells as part of enhanced oil (Bruckdorfer, 1986) or coal bed methane (Kumar et al., 2014) recovery, engineered and CO$_2$ plume geothermal systems (Randolph & Saar, 2011), and permanent carbon storage efforts (Zhang & Bachu, 2011). This multiplicity generates broad appeal for understanding CO$_2$-mediated changes to the physical and chemical properties of any geomaterial in the subsurface acting as a fluid barrier.

One example of a barrier is wellbore cement, which must confine CO$_2$ during injection processes related to enhanced recovery or sequestration. Natural formations that effectively seal in CO$_2$ from above—sometimes referred to as caprocks—include evaporites, shales, and clay-rich mudstones (Espinoza & Santamarina, 2017; Song & Zhang, 2013). Yet another possible barrier to CO$_2$ has been identified within the Campi Flegrei caldera. It is a consolidated and altered volcanic ash bed with fibrous and platy minerals woven into the rock
matrix (Vanorio & Kanitpanyacharoen, 2015). One of these, tobermorite, is a calcium-silicate-hydrate (C-S-H) that occurs naturally in hyper-alkaline, hydrothermal environments (Rochelle & Milodowski, 2013; Shaw et al., 2000) but is best known as a group of gels and crystals that bind together modern and ancient cement-based building materials (Jackson et al., 2017). Such cementitious materials react chemically with CO2 and undergo changes in porosity and permeability (Reardon et al., 1989). Since CO2 is the second most plentiful gas at fumaroles near Campi Flegrei (Caliro et al., 2007), the volcaniclastic tuffites possessing C-S-H minerals may experience changes to permeability that are similar to those observed for engineered cements and concretes. This is an important claim to verify given that the permeability of lithologies in rock physics models, although tunable, are usually assigned fixed values in time. Since permeability influences overpressure in the system, which in turn influences ground surface deformation, time-dependent values are necessary in order to accurately correlate symptoms of unrest, for example, increased seismicity, altered gas emissions at fumaroles, and uplift (Todesco, 2008).

In this paper we focus on how chemical and physical mechanisms involving CO2, which is abundant in many volcanic areas (Lowenstein, 2001), can change the permeability of a consolidated ash bed while migrating up the geologic column. Two processes are examined that have yet to be deeply explored in the literature on hydrothermal systems: mineral carbonation and rapid depressurization. Below we present in situ gas permeability measurements during the carbonation (i.e., mineralization of CO2) of partially water-saturated, hydrostatically confined, plugs of ash-based cement and concrete (i.e., cements containing course aggregates). The cementitious material within our samples is a fine gel of C-S-H that forms when the amorphous silica in volcanic ash reacts with hydrated lime. Our findings also include the subsequent changes to permeability upon rapid or gradual release of CO2 pore pressure using different boundary conditions. Furthermore, we provide data from time-lapse and postmortem X-ray powder diffraction (XRD), X-ray computed tomography (XCT), and scanning electron microscopy (SEM) in order to correlate the evolution of permeability with mineralogical, macrostructural, and microstructural changes. Our results reveal how carbonation and depressurization can influence the sealing properties of low permeability, lime-cemented, volcanic sediments.

2. Background

Mineral carbonation occurs when CO2 gas dissolves into the adsorbed or capillary (or in select cases, bound) water of a solid containing metal oxides or silicates (or hydrates of these) and triggers a chemical reaction that produces carbonate salts. There is a large body of literature on the carbonation of cement, concrete, mortar, and cement-solidified hazardous waste stemming from efforts to enhance the durability of construction materials and reduce carbon footprints (Ashraf, 2016; Bertos et al., 2004; Hossain et al., 2016; Šavića & Luković, 2016). The two constituents of modern cement mixes that are usually inspected are calcium hydroxide (i.e., portlandite, slaked lime, or hydrated lime) and C-S-H. Their respective carbonation reactions can be represented by the following equations:

$$Ca(OH)_2 + CO_2(aq) \rightarrow CaCO_3 + H_2O$$  

(1)

$$\left(CaO\right)_x\left(SiO_2\right)_y\cdot \left(H_2O\right)_z \rightarrow xCaCO_3 + ySiO_2 + \left(H_2O\right)_z + (z - y)H_2O$$  

(2)

where the precise stoichiometry of the second reaction is not necessarily known due to the complexities of C-S-H decalcification and silica gel hydration (Morandeau et al., 2014). In both cases the precipitation of calcium carbonate (CaCO3) into the pore space changes local porosity, permeability, elasticity, and strength. Research on Portland cement, the most ubiquitous cement today, suggests that it remains relatively impermeable under static wellbore conditions (Carey, 2013; Zhang & Bachu, 2011), although there are few studies reporting in situ flow or permeability data during carbonation of confined, intact specimens (Bachu & Bennion, 2009; Dewaele et al., 1991; Laudet et al., 2011; Martin, 1986; Purser et al., 2014; Sweatman et al., 2009). Still, it has been shown that CaCO3 fills porosity and can heal fractures and cement-rock interfacial defects under a range of experimental conditions (Carroll et al., 2016). As a result some have proposed to leverage carbonation in order to enhance wellbore cement (Lee et al., 2016), repair seal-compromised reservoirs (Ito et al., 2014), and otherwise control permeability in the subsurface (Tao et al., 2016).
The carbonation of cement and concrete also depends on the presence of supplemental cementitious materials, which are additives that reduce costs and/or improve certain engineering qualities such as resistance to chemical attack. Some common substances include volcanic ash, industry byproducts (e.g., blast furnace slag), and other pozzolanic materials, that is, siliceous or aluminous-siliceous agents that react with hydrated lime. Pozzolanic concretes may be even closer cousins to hydrothermally altered ash beds than pure Portland cement, in that they contain volcanic lithics or analogs thereof. Reviews on the interaction of these hybrids with CO₂ highlight a divergence in the research (Ashraf, 2016; Hossain et al., 2016), with claims that the supplements to a cement mix can enhance, diminish, or maintain levels of carbonation resistance (i.e., CO₂ impermeability). Likewise, inconsistencies have surfaced within the literature on human-driven carbon capture in rocks, for example, concerning CO₂ interactions with basalt and ultramafic formations (Olajire, 2013). We simply highlight two of these: The invariability of the elastic rock frame during carbonation is an insufficient assumption for interpreting time-lapse seismic data (Adam et al., 2013), and reaction rates can sometimes be much faster than those predicted (Matter et al., 2016). Given that pozzolanic concretes are comparable in composition to consolidated ash beds, more clarity regarding changes in the permeability of such geomaterials can serve the engineering and earth science communities alike.

The second process that we examine here is comparable to rapid decompression, that is, when the pressure outside of a sample is suddenly reduced so that entrained fluids expand and generate internal stresses on the pore network. Laboratory analogs of eruptive processes have demonstrated that pyroclastic rocks fragment during the rapid expansion of flashed steam (Montanaro et al., 2016) and argon gas (Montanaro et al., 2016; Spieler et al., 2004), the latter of which has a similar expansion ratio to CO₂ at certain pressures and temperatures. Although these results may relate to, for example, hydrothermal/geothermal well-field explosions triggered by hydraulic fracturing or seismicity associated with high-pressure gas collected in locally fractured areas (Hedenquist & Henley, 1985), it is unclear how to apply them to deeper rocks experiencing greater lithostatic stress. It is possible that, if the arising stress gradients are sufficient, a sudden expansion of pore fluid following the partial or total failure of rocks providing a seal causes further damage to the formation. To our knowledge there are no experiments probing the specific character of CO₂ depressurization in rocks under stress, whether from geothermal fields, volcanoes, or calderas (nor in wellbore cement despite the large pressure swings during CO₂ injection).

3. Materials and Methods

A schematic of our workflow on intact samples is provided in Figure 1. For the purposes of this study, four samples of cemented volcanic ash (CVA1–4) and one concrete sample (CVA5c) were manufactured. The production process enabled us to consistently reproduce rock-like plugs and therefore keep the mineralogy, microstructure, and macrostructure approximately fixed as parameters. The four cement samples were cast and cured from a single mix of tap water (118 g), aged lime putty (99 g) from Cimmino Calce, and a highly amorphous and reactive volcanic ash (202 g) from a quarry near Campi Flegrei that was sieved to 177 μm. X-ray fluorescence of the ash identified silicon, aluminum, and potassium as the major elements therein, and XRD revealed the major crystalline components to be alkali feldspars (e.g., sanidine) and analcime (see the supporting information). The methods for casting and curing were similar to those of Collepardi et al. (1976). The sieved volcanic ash was humidified with 20 g of the water by thoroughly mixing and leaving in a closed container for 3 days. Afterward, the lime putty was diluted in the remaining water and mixed with the damp ash. The slurry was poured into cylindrical molds machined from chlorinated polyvinyl chloride and uniaxially pressed with 1 MPa for 15 min. Some water was released from the slurry at this time, resulting in a final water-to-cement ratio of 0.33. The compacted samples in their molds were placed above a water bath in a closed chamber for 18 hr during their initial set at room temperature. The system was subsequently ramped to 70 °C over 2 hr. The curing temperature was maintained for 28 days, during which time samples were subjected to 100% relative humidity. At the end of this period the chamber was allowed to cool to room temperature overnight. Plugs, 25 mm diameter by 50 mm length, were removed from the molds and stored in water-filled, polypropylene centrifuge tubes prior to drying. The concrete sample (CVA5c) underwent a slightly different production protocol due to it being from an earlier
generation of fabricated samples: (i) deionized water was used; (ii) ash came already humidified and was sieved to 1.4 mm; (iii) aggregates of Neapolitan Yellow Tuff sieved to 1.4 mm were added (20% of the total mixed mass); (iv) the mold was a greased, metal split cube that separated from the plug prior to steam treatment; (v) a higher packing pressure of 2 MPa (yielding a water-to-cement ratio \(< 0.3\)) and curing temperature of 99 °C were employed; (vi) the plug was placed in and removed from a preheated steam chamber; and (vii) the final sample length was approximately 25 mm.

Samples CVA1 and CVA5c were completely dried and used in the preliminary characterization of the following rock physical properties: grain density ($\rho_G$), dry porosity ($\phi$), permeability ($k$), and ultrasonic P wave ($V_P$) and S wave ($V_S$) velocities. The dry mass of these plugs was defined as the stabilized value acquired after several days in an oven at 80 °C. Our concrete sample (CVA5c) was used first in all the experiments, and therefore served as a test plug. Subsequently, slight adjustments were made to some of the methods for the cement samples. While CVA5c was dried for 7 days at 80 °C, CVA1 underwent more gradual steps in order to better preserve the C-S-H microstructure (Zhang & Scherer, 2011): 2 weeks at room temperature, 4 weeks at 45 °C, and 5 days at 80 °C. The volume of solid material, or grain volume ($V_G$), for both CVA1 and CVA5c was measured with a helium pycnometer by expanding gas into the pore space from a known volume at an initial pressure of 0.6 MPa. The grain density and dry porosity were then calculated from the $V_G$ value using the dry mass and bulk volume ($V_B$), respectively. Benchtop, ultrasonic P wave (1.0 MHz) and S wave (2.25 MHz) velocities were also acquired for these samples in the dry condition from pulse time-of-flight measurements using pairs of contact transducers (12 mm in diameter) powered by a 5055PR, all manufactured by Panametrics. Acoustic coupling between the transducers and samples was aided by a high viscosity bonding medium (Clark & Vanorio, 2016). A relatively low water saturation ($S_w$) for CVA5c was used in the initial test runs of our carbonation and depressurization setup and was obtained through re-equilibration with ambient relative humidity (~55%) in the laboratory. To simplify the hydraulic history of the remaining plugs, which is known to alter the permeability of concrete (Villar et al., 2015), samples CVA2–4 were partially dried at room temperature until reaching the desired water saturations. Since this method did not allow for the characterization of the dry state, the grain
density of CVA1 ($\rho_G = 2,400 \text{ kg/m}^3$) was assumed to be representative of CVA2–4 and was used in the estimation of $S_w$ values (in percentage of pore volume) according to the relation,

$$S_w = \frac{100 \rho_w}{\rho_B} \frac{m_w - V_B \rho_B}{V_B - V_B \rho_B}$$

where $\rho_w = 1,000 \text{ kg/m}^3$ for water, $\rho_{B, sat}$ is the bulk density of each sample upon removal from the steam chamber (assuming $S_w = 100\%$), $m_w$ is the measured mass of each partially dry sample, and the fraction with $V_B$ as its coefficient is the estimated grain volume for each cement plug.

Samples were inspected by SEM before and after the carbonation and depressurization experiments. Backscattered electron micrographs of sample surfaces were taken using a Hitachi S-3400 N VP-SEM. A beam intensity of 15 keV and a vapor pressure of 50 Pa enabled good resolution without a metal coating, thereby maintaining a sample surface reactive to CO$_2$. Furthermore, a cross section from one sample (CVA2) was analyzed with a JEOL JXA-8230 electron microprobe at the end of the experiment. The sample surface was carbon coated following two polishing steps with silicon carbide sandpaper, beginning with 600 grit (10–40 $\mu$m) and ending with P2000 (10 $\mu$m). Elemental maps of the cross section were obtained through energy-dispersive spectroscopy (EDS) of the X-rays emitted from the surface upon excitation by a 20-keV electron beam. A silicon drift detector counted X-rays point by point using a 2-ms dwell time. Full scans at each site of interest were acquired five times consecutively, such that mapping of an area typically required 2 hr.

XCT using a Zeiss Xradia Versa 520 was also performed in a time-lapse fashion. Whole plug scans were obtained using a polychromatic beam centered at 140 keV, the lowest energies of which were removed by a Zeiss software, with which the center shift and beam hardening constants were tuned. Tomographic data sets for each plug were attained by vertically stitching together two (CVA5c) or three (CVA2–4) successive reconstructions that overlapped in height by approximately 50%. The final, reconstructed pixel size was around 30 $\mu$m, which enabled three-dimensional visualizations of large-scale mineral precipitation and fracturing. Data exploration and analysis were conducted using both Dragonfly 3.1 (Dragonfly, 2016) and ImageJ 1.51n (Schneider et al., 2012) on a Dell workstation running Windows 7.

Helium and CO$_2$ gas permeabilities ($k_d$) of samples were quantified with an Automated Nano-Darcy Permeameter NDP-605 from CoreTest Systems, Inc., using the pulse-decay technique according to the formula,

$$k_d = B \frac{d}{dt} \ln(\Delta P_p(t)),$$

where $B$ is a constant containing system volumes, sample dimensions, and gas properties; and $\Delta P_p(t)$ is the amplitude of the transient pore pressure pulse (Jones, 1997). A schematic of the setup is depicted in Figure 2. Pulse amplitudes of 0.04 and 0.1 MPa were applied on top of the mean pore pressure ($P_m$) for each helium and CO$_2$ datapoint, respectively, using a pneumatically driven pulse generator. A pressure intensifier converted compressed air to the water-mediated confining pressure ($P_c$) that was hydrostatically applied through equivalent pressures from the top piston (axial) contacting the sample and rubber jacket (radial) around it. Samples were additionally wrapped with 2 layers of aluminized mylar in order to minimize diffusion of CO$_2$ through the rubber jacket. The instrument maintained a core holder temperature of $T = 33 ± 0.1$ °C and differential pressure of $P_d = P_c - P_p = 5 ± 0.1$ MPa during all measurements. In order to compare permeabilities with those found in the literature that were acquired with water or brine, the helium pore pressure was varied incrementally through $P_p = 1, 2, 5,$ and 10 MPa steps and the permeability was computed via the Klinkenberg (1941) correction.

Although the results of this study have wider application, we aligned the pressure conditions of the permeameter with estimates from the Campi Flegrei caldera in order to be tethered to an example in the subsurface. Since there are limited data from the wells drilled within the caldera, the Mofete geothermal wells in the west were taken into consideration. The partial pressure of CO$_2$ was measured to be 2.6 MPa in Mofete 1 at 1606 m and 5.1 MPa in Mofete 2 at 1989 m (De Vivo et al., 1989; Guglielminetti, 1986). We therefore decided on a CO$_2$
pore pressure of $P_p = 5$ MPa. The differential pressure was taken as a conservatively low estimate of the effective stress on the C-S-H-bearing rock layer positioned at 1.5–2.5 km depth within the caldera (Vanorio & Kanitpanyacharoen, 2015). This was computed from estimates of the overburden and total pore pressures. First, for the overburden, we chose an average dry bulk density of 1300 kg/m$^3$ and dry porosity of 43% for the overlaying tuffs (Vanorio et al., 2002). Based on those values, we calculated a wet bulk density of 1,700 kg/m$^3$ that corresponds to complete water saturation. We then assumed that approximately 0.5 km of that depth is dry, and the remaining 1–2 km are fully saturated, somewhat resembling the multireservoir scheme offered by Guglielminetti (1986). The densities, multiplied by the gravitational constant and their respective depths (totaling 1.5–2.5 km), yielded a range in lithostatic pressure of 23–40 MPa. Note that using slightly different densities over these depths influences the calculation, for example, numbers from Barberi et al. (1991) yield 30–52 MPa. Second, a hydrothermal reservoir pressure of 10–20 MPa was supposed on the basis of CO$_2$ concentrations of a few percent (De Vivo et al., 1989; Guglielminetti, 1986) and phase equilibria of the H$_2$O-CO$_2$-NaCl system (Dubacq et al., 2013). Taking the upper and lower limits of pore and lithostatic pressure, respectively, yields $P_d = 23 - 20 = 3$ MPa. Given the large uncertainty in such approximations (e.g., numbers from Barberi et al., 1991, produce $P_d = 10$ MPa), we chose $P_d = 5$ MPa.

Samples remained under hydrostatic $P_c = 10$ MPa throughout the carbonation stage of each experiment, which was carried out within the permeameter following helium permeability measurements. That is, after slowly venting helium from the pore space samples were re-pressurized from both ends with CO$_2$ gas at $P_p = 5$ MPa. Then a saturation stage of one to several hours ensued, during which time pore pressure stabilized. Samples began to carbonate immediately upon exposure to the CO$_2$ gas, which was monitored through the periodic assessment of gas permeability for 120–400 hr.

CO$_2$ in the pore space was depressurized to atmosphere under various conditions in order to simulate different processes in the subsurface. Sample CVA2 experienced slow depressurization over 1 hr while confining pressure was held constant at $P_c = 10$ MPa, thus mimicking the slow seepage of CO$_2$ out of a host rock. This sample alone was exposed to a second round of carbonation and then rapidly depressurized (with $P_c = 10$ MPa) by fully opening the bypass and vent valves in the pore line (see Figure 2). The venting process took a few seconds as 250 ml of CO$_2$ gas in the pore line exited to atmosphere through a long capillary (1 mm inside diameter by 1 m length). This process is analogous to faulting, where the escape of entrained CO$_2$ is facilitated by the opening of an alternative pathway. The depressurization of samples CVA3 and CVA4 was
Table 1
Grain Density, Porosity, Liquid Permeability, and Ultrasonic Velocities of Samples Before and After Carbonation and Depressurization

| Sample       | $\rho$ (kg/m$^3$) | $\Phi$   | $k$ ($10^{-18}$ m$^2$) | $V_p$ (km/s) | $V_S$ (km/s) |
|--------------|-------------------|----------|------------------------|--------------|--------------|
| CVA1 (pre)   | 2,400             | 0.360    | 6.0                    | 3.057        | 1.794        |
| CVA5c (pre)  | 2,270             | 0.296    | 2.1                    | 2.755        | 1.853        |
| CVA2 (post)  | 2,460             | 0.335    | -                      | 2.511        | 1.600        |
| CVA4 (post)  | 2,450             | 0.308    | -                      | 2.693        | 1.673        |
| CVA5c (post) | 2,340             | 0.256    | 4.2                    | 2.499        | 1.666        |

Note: All measurements were carried out on dry samples with the exception of CVA5c permeability (pre $S_w = 12\%$ pre, and post $S_w = 18\%$). The initial porosities of CVA2, CVA3, and CVA4 were estimated, respectively, to be 0.360, 0.353, and 0.359 based on their calculated grain volumes (see equation (3)). Thus, the permanent loss of porosity in CVA2, CVA4, and CVA5c were estimated as 0.025, 0.045, and 0.04, respectively. The relative uncertainties for $\rho$, $\Phi$, and each velocity from this study are less than 0.5%, 1.5%, and 1%, respectively. Permeability errors for CVA1 and CVA5c were 1 and $0.1 \times 10^{-18}$ m$^2$, respectively. CVA = cemented volcanic ash.

4. Results

4.1. Initial Characterization of CVA

Some physical and elastic properties of CVA1 and CVA5c are shown in Table 1. The inclusion of lightweight aggregates in CVA5c resulted in a lower grain density than CVA1, whereas porosity and permeability values were most heavily influenced by packing pressure during casting and ended up similar to those measured for Portland cements cured under wellbore downhole conditions (Fabbri et al., 2009; Rimmelé et al., 2008). For example, Fabbri et al. (2009) gave values of $\Phi = 0.41$, $k_g = 7.1 \times 10^{-18}$ m$^2$, and $k = 1.0 \times 10^{-18}$ m$^2$, while Rimmelé et al. (2008) reported $\Phi = 0.33$ and $k < 8 \times 10^{-18}$ m$^2$. The $P$ wave velocity of the CVA (CVA1) is approximately 15% lower than that of Portland cement, but the $S$ wave velocity is only 6% less (Fabbri et al., 2009). Compared to ash beds in Campi Flegrei, the samples from this study possess higher porosity and yet similar permeability, that is, versus $\Phi = 0.2$ and $k = 2–30 \times 10^{-18}$ m$^2$ (Vanorio & Kanitpanyacharoen, 2015). The discrepancies between CVA1 velocities and Campi Flegrei rocks were larger than those with Portland cement, although much of the difference can be explained by the larger porosity. The velocity was 7–20% less for $P$ waves and 14–23% less for $S$ waves (Zamora et al., 1994).

Common microstructural features found in the samples are depicted in Figure 3. SEM of sample faces revealed that plugs primarily consisted of volcanic glass fragments ranging in size from a few microns to a few hundred microns. These were bound together by a fine gel of C-S-H with textural features that were usually submicron, although longer needles or fibers were also present. Other entities included dense laths containing iron and titanium, as well as unincorporated, millimeter-sized bodies of microcrystalline lime that had only reacted with the ash at their boundaries. These observations are consistent with XRD data from CVA1 (see Figure 3g), which detected lime (i.e., portlandite) as well as the sandine and analcime minerals.
in the ash. The broad peak in the XRD curve is likely due to the abundance of volcanic glass. The C-S-H minerals, which are sometimes described as X-ray amorphous because they possess relatively few diffraction maxima that are broad and weak (Grangeon et al., 2013), were undetectable (as would be any amorphous products from the carbonation of the C-S-H; Ashraf, 2016). On the macroscale, cross sections of whole plugs reconstructed from XCT prior to carbonation and depressurization demonstrate that unreacted samples were fairly homogeneous in density throughout the bulk of their volume (see Figure 4a).

4.2. Time-Lapse Observations

Rock physical properties for CVA2, CVA4, and CVA5c after carbonation and depressurization are given in Table 1. Estimated initial porosities for CVA2–4 are stated in the caption for comparison. It was discovered that, while the porosity of CVA5c decreased due to the formation of carbonate minerals, the final
permeability doubled and the velocities fell by 10%. Nearly identical relative changes to velocity occurred in CVA4, assuming its initial $V_P$ and $V_S$ were similar to CVA1. The $P$ wave velocity for CVA2 suffered the worst fate, slowing by ~18%.

**Figure 4.** X-ray computed tomography reconstructions of samples. For all images, gas flow during permeability measurements was from bottom to top. Slices from the $xz$ plane refer to CVA2 (a) before and (b) after carbonation and slow/confined depressurization, as well as (c) CVA3 and (d) CVA4 following carbonation and rapid/unconfined depressurization (i.e., decompression). The histograms below CVA2 images were obtained for the two different three-dimensional volumes marked by the white boxes drawn with either solid or dotted lines, which match the corresponding line styles in the graphs. Fractures (red arrows) in the outer carbonated zone of samples depressurized with and without confining pressure exhibited different patterns. High-magnification images of CVA2 after the (e) first and (f) second experimental runs and (g) upon oven drying highlight in the $yz$ plane the intersection of the reaction rim and a fracture. CO$_2$ diffused from the outer to the inner zone during permeability tests. CVA = cemented volcanic ash.
Figures 4a and 4b illustrate how the originally uniform density of sample CVA2 evolved. A phase contrast between the outer and inner regions of the plug was observed by XCT after carbonation and depressurization (Han et al., 2013; Jung & Um, 2013; Kutchko et al., 2009). Histograms of X-ray intensity for a 0.5 cm³ volume from the inner portion indicate that less transformation occurred there (see Figure 4b, black and red dotted lines). The main difference was a horizontal shift to lower grayscale values, which we can partly attribute to the evaporation of several grams of pore water during SEM prior to XCT. On the contrary, histograms for a 1 cm³ volume from the outer region show that the peak for this zone not only shifted but also narrowed and grew in amplitude (see Figure 4b, black and red solid lines). The differences between the two zones will be described in more detail below (see Figure 5).

Figures 4c and 4d show the XCT reconstructions of samples that experienced rapid decompression. CVA3 served as a “twin” to sample CVA2 by starting with a nearly identical water saturation and being carbonated for a similar duration. Consequently, the same three-dimensional pattern of carbonation (see Figure 4b) was reproduced, that is, a large interior volume of slightly modified cemented ash containing pore water and surrounded by a heavily carbonated region. The striking difference between Figures 4b (CVA2) and 4c (CVA3) is the presence of multiple vertical fractures in the latter. Note that none of the fractures following depressurization extended into the inner zone that remained water saturated. Sample CVA4 in Figure 4d was the most extensively fractured.

Of particular interest is the reaction front displayed at higher magnification in Figures 4e–4g. Close inspection of the sequence reveals that the leading tip of the reaction rim possesses an X-ray intensity slightly elevated from that of the surrounding matrix (see also Figure 5). Recall that this plug underwent partial dehydration during SEM and resaturation prior to the second run (see Figure 1). The drying left much of the water saturation intact in the central volume, unlike in the outer zone where porosity in the form of macropores is readily discernible (see Figure 4b, black circles). The high water retention within the reaction rim means that it acted as a liquid barrier. Further advance of the reaction into the core of the sample during the second run was fairly even along the boundary, resulting in a second reaction rim nearly parallel to the first. The one exception is an extensive infiltration of CO₂ that occurred at the intersection of the original rim and a fracture in the outer region. This was the case along the entire junction of the rim and fracture, the latter of which existed as a nearly horizontal crack spiraling around a portion of the central volume (i.e., the two red arrows in Figure 4b denote the same helical fracture). The cracks that arose in CVA2 following oven treatment at the end of the experiment were found only within the inner zone (see Figures 4g and S3d) and were probably caused by drying shrinkage (Chatterji, 1976). They are likely the cause of the severe P wave velocity decrement for this sample (see Table 1).

Elemental maps of one CVA2 slice featuring the inner and outer zones adjacent to the reaction rim are presented in Figure 5. Besides oxygen, the most abundant elements detected with EDS are silicon (red), calcium (green), and aluminum (blue), here listed from greatest to least. The silicon and aluminum came from the volcanic ash, while the large calcium content was mostly sourced by the lime (see Table S1). Calcium was found in high concentrations in the outer zone and at the reaction rim, appearing to have separated from, and coalesced around the aluminous-siliceous regions (magenta). Apart from those associated with carbonated lime bodies, high intensity signals associated with were less common within the reaction rim. On the other hand, XRD traces for CVA2 subsamples from the two zones are quite similar (see Figure 5c). From these data we know that all of the lime transformed into carbonate phases, regardless of location. Thus, it appears that the contrast between zones in XCT reconstructions and EDS maps is associated with a difference in the extent to which C-S-H carbonated (and note that amorphous carbonation products would not show up in XRD; Ashraf, 2016). Indeed, the preferential carbonation of lime over C-S-H has been reported in numerous studies on engineered cements and is known to vary depending on environmental conditions, CO₂ concentration, time, and C-S-H structure (Šavija & Luković, 2016).

4.3. Permeability Evolution

Figure 6 depicts the time-dependent gas permeability for the cement and concrete samples during the carbonation process. Data obtained with helium (large symbols) at the same pore pressure show some discontinuities with CO₂ data, that is, the initial kₚ values were always less for helium gas than for CO₂. Given that both gases are susceptible to relative permeability effects from two phase flow, the
Figure 5. Examination of the elemental phases of CVA2 and crystalline phases of CVA2 and CVA4 after carbonation. (a) Approximate locations of energy-dispersive spectroscopy analysis on CVA2 are given in the xy plane of the X-ray computed tomography reconstruction. (b) Silicon (red), calcium (green), and aluminum (blue) are displayed using a three-color scheme, such that the aluminous-siliceous ash looks magenta. The unincorporated lime that carbonated shows up as bright green masses in both zones. Calcium at the reaction rim and outside of it was typically found in higher concentrations and segregated from the aluminous-siliceous phase. On the contrary, it was more evenly distributed within the rim (i.e., the green and magenta colors were less bright and distinct). A grayscale version of the calcium map is also displayed for one of the regions, in which a lower threshold has been set to highlight the areas of high calcium content. (c) X-ray powder diffraction data for two CVA2 subsamples and one CVA4 subsample demonstrate the absence of lime after carbonation was carried out. The amorphous background has been subtracted, and all curves were normalized by the largest peak at $2\theta = 29.5^\circ$. The identified diffraction maxima are labeled as follows: "S" for sanidine, "A" for analcime, "C" for calcite, and "V" for vaterite. The best match for calcite was a reference containing trace impurities (i.e., 3% magnesium vs. 97% calcium). Data obtained from the inner and outer zones of CVA2 are very similar. However, the normalization to calcite results in slightly smaller intensities for the sanidine and analcime peaks, which should have equal abundance for all cement samples. The biggest difference is found when comparing CVA2 and CVA4, the latter of which contains more vaterite. CVA = cemented volcanic ash.
discrepancy at early times is best explained by an enhanced decay of CO2 pressure due to its solubility in water. Regardless, the measured CO2 gas permeability steadily declined during carbonation, appearing to follow a power law within certain intervals (see Table 2). Ultimately, the gas permeability dropped by more than one order of magnitude in samples containing the most water. The results are consistent with the limited data in the literature on Portland cement. For example, Sweatman et al. (2009) noted that the flow of humidified CO2 gas through an uncracked specimen of Portland cement (with initial \( k_0 = 2.6 \times 10^{-17} \text{ m}^2 \) using nitrogen) quickly became undetectable despite a pore pressure gradient of 3.5 MPa. Dewaele et al. (1991) quantified the CO2-rich water permeability of grout (i.e., Portland cement plus quartz sand) while varying the effective stress state, finding \( k = \sim 10^{-17} \text{ m}^2 \) to diminish to \( \sim 10^{-20} \text{ m}^2 \) during carbonation. Likewise, neat cements have been shown to become less permeable to both CO2-rich brine (i.e., from \( k = 2 \times 10^{-19} \) to \( 1 \times 10^{-20} \text{ m}^2 \); Bachu & Bennion, 2009), and CO2-rich water for a sample under deviatoric stress (i.e., from \( k = 1.6 \times 10^{-18} \) to below the measurement limit; Laudet et al., 2011). Data taken from Bachu and Bennion (2009) are plotted in Figure 6 for comparison.

Relative to the initial helium permeability, rapid decompression of CVA4 (large green circles) led to an increase in permeability by a factor of five, while it nearly doubled for CVA5c (large gray squares) after its depressurization at fixed \( P_d = 5 \text{ MPa} \). Note that the helium permeability for sample CVA2 (large red crosses) following slow/confined depressurization remained low, having a final reduction around 40-fold from its precarbonation value. On the contrary, CVA3 (large yellow triangles) was submitted to decompression and exhibited a factor of four increase from its initial helium permeability (and strikingly, this was 111 times the \( k_0 \) value for CVA2 after its first round of depressurization). Similar ratios as those listed above also describe the changes in the Klinkenberg-corrected permeability (see Figure S4).

Lastly, the second iteration (red asterisks) of experiments on CVA2 produced a CO2 permeability near the lower limit of our permeameter within 24 hr of carbonation, and a slight decrease in helium permeability relative to its second starting value (see Figure 6, red asterisk near 200 hr) after rapid/confined depressurization. The release of pore pressure in this instance did not induce fractures. Rather, some water (0.28 g) was expelled from the pore space into the gas lines of the permeameter.

5. Discussion

5.1. Understanding the Minutia

We begin our discussion by establishing an understanding of the physical changes to the samples following carbonation and depressurization. All plugs gained 8–11% of their measured (CVA5c) or estimated (CVA2–4) dry mass prior to experiments. We argue that this is a direct measure of the CO2 mineralized within each sample. If true, the mass increase \( (dm = m_{post} - m_{pre}) \) from the experiment should be proportional to the mass of released H2O \( (m_{release}) \) specified in equations (1) and (2). To explicitly test this, we measured the total mass loss \( (m_{loss}) \) in reacted samples from oven drying at 80 °C. This decrement was equal to the mass of all the free water that remained in the pore space after carbonation and depressurization. In theory, the \( m_{loss} \) value is equivalent to the sum \( (m_{sum}) \) of the initial water mass that partially saturated the pore volume \( (m_v) \) and that which was released during carbonation.
the Klinkenberg-corrected value) was recovered during the processes of partial drying and resaturation. However, since local humidity levels tend to increase as $\text{H}_2\text{O}$ is released, the extent of gas permeability in these regimes is also compatible with previous carbonation studies on unconfined cements. For instance, carbonation is most extensive when relative humidity is $50\% - 60\%$ (Galan et al., 2013). However, since local humidity levels tend to increase as $\text{H}_2\text{O}$ is released, the extent of gas permeability during carbonation has been boosted by alternating between periods of $\text{CO}_2$ injection and drying to mitigate pore clogging (Phung et al., 2015; Reardon et al., 1989). Furthermore, the starting $\text{CO}_2$ permeability of sample CVA2 in the second carbonation run con

It is also helpful to quantify the changes in porosity due to $\text{CO}_2$ uptake. A comparison of the dry porosities of select plugs before and after experiments proves that there was a permanent loss in the connected porosity of approximately $0.025 - 0.045$ (see Table 1). The largest numbers are associated with samples of low water saturation, presumably because there was greater access to reactive minerals. However, since all the lime carbonated, the mitigation of carbonation in samples with higher $S_w$ values must have been primarily limited to the C-S-H phase. Lastly, note that the pore filling from released $\text{H}_2\text{O}$ (see equations (1) and (2)) was ascertained from changes in water saturation and found to be approximately $0.05$ for CVA5c and $0.065 - 0.08$ for the others. Having these numbers in hand, we move on to the permeability results.

5.2. Barriers and Their Permeability

As previously mentioned, very few in situ permeability data exist in the literature due to the practical challenges of measuring and interpreting the changes during carbonation. However, there is general consensus that the permeability of Portland cement-based systems decreases during carbonation due to pores filling with $\text{CaCO}_3$ (Ashraf, 2016; Carey, 2013; Šavija & Luković, 2016; Zhang & Bachu, 2011). The precipitant tends to form a continuous layer near the surface of plugs submerged in water. In the event that the cement is not fully saturated, gas transport is possible and the gas permeability is not only affected by $\text{CaCO}_3$ formation, but also by the release of $\text{H}_2\text{O}$ into the pore space (Phung et al., 2015; Reardon et al., 1989). Accordingly, in the previous section we computed the relative contributions of the reaction products, $\text{CaCO}_3$ and $\text{H}_2\text{O}$, to the porosity loss during carbonation. How these relate to gas permeability will now be outlined.

The swift decline of $\text{CO}_2$ permeability during carbonation observed in samples with high initial $S_w$ values demonstrates that $\text{H}_2\text{O}$ could effectively reduce the cross-sectional area available to gas at the outset. Such a claim is consistent with the fact that $S_w = 80\%$ can entirely obstruct gas flux through ordinary concrete (Kameche et al., 2014). This sensitivity to water saturation is also compatible with previous carbonation studies on unconfined cements. For instance, carbonation is most extensive when relative humidity is $50\% - 60\%$ (Galan et al., 2013). However, since local humidity levels tend to increase as $\text{H}_2\text{O}$ is released, the extent of carbonation has been boosted by alternating between periods of $\text{CO}_2$ injection and drying in order to mitigate pore clogging (Phung et al., 2015; Reardon et al., 1989). Furthermore, the starting $k_g$ value (see Figure 6, red asterisks) for CVA2 in the second carbonation run confirms that a significant fraction of the permeability decrement following the first run was impermanent. In fact, an order of magnitude in gas permeability (and the Klinkenberg-corrected value) was recovered during the processes of partial drying and resaturation. These facts suggest that $\text{H}_2\text{O}$ was the dominant suppressor of gas permeability in our study.

Given the comparable magnitudes of the temporary and permanent porosity losses due to $\text{H}_2\text{O}$ and $\text{CaCO}_3$, respectively, the higher sensitivity of gas permeability to $\text{H}_2\text{O}$ probably reflects where it deposited during carbonation. SEM of sample surfaces revealed that $\text{CaCO}_3$ was ubiquitous throughout the reacted matrix, but many of the micron-sized crystals or amorphous bodies that were produced from carbonation were not joined together to form a continuous layer (see Figures S1 and S2). Rather, the mineral formation in these regions of relatively low water saturation appear to be limited in function to reducing pore radii (Goñi et al., 2002; Reardon et al., 1989; Rimmelé et al., 2008). Thus, although they result in a tighter
While the presence of water within our samples likely affects the capillary entry pressure, so does the pore structure itself. Data gathered from the literature demarcates an inverse relationship between breakthrough pressure and pore size in rocks, with maximum values for CO₂ on the order of 1–10 MPa in formations with permeabilities in the range, 10⁻²¹ to 10⁻¹⁷ m² (Espinoza & Santamarina, 2017). Similarly, well cement has been shown to sustain CO₂ shut-off pressures (i.e., the stabilized pressure gradient after gas dissolution, diffusive transport, and phase flow have ceased) from 1 to 6 MPa (Kim & Santamarina, 2013; Sweatman et al., 2009). Given these numbers it is not surprising that the CO₂ permeability from this study, measured with a small ΔP_p (t = 0) = 0.1 MPa, tended to zero as pores clogged with reaction products. Altogether, it appears that a rock containing C-S-H or other minerals susceptible to carbonation will undergo pore size reduction, enhancing its ability to serve as a fluid barrier. This conclusion can be contrasted with the work of Crow et al. (2010), who measured capillary pressures of cement plugs taken from a 30-year-old well located in a natural CO₂ reservoir. They found with a centrifuge method that highly carbonated cores, versus slightly carbonated ones, were less prone to resisting the displacement of brine by air. However, interpretation of their results is complicated by very different porosities and permeabilities in the slightly carbonated and highly carbonated samples.

Our discussion thus far has focused on the heavily carbonated, outer zone of the plugs. However, the most effective barrier to species migration could be the enclosing rim of CaCO₃ around water-saturated regions (see Figures 4b, 4c, 5b, and 5c). This notion is supported by two observations. First, regarding CO₂ mobility across the reaction rim, the lack of fractures in the central volume of CVA3 following decompression supports the notion that little or no CO₂ gas expanded from within that region as depressurization was carried out. This means that diffusion of CO₂ toward the center of samples was slowed by the CaCO₃ rim, such that the inner zone was ultimately infiltrated by lesser quantities of CO₂ than the outer one. Second, regarding water traversing the barrier, histograms from XCT reconstructions verify that CVA2 primarily dehydrated under SEM vacuum only in the outer carbonated zone (see Figure S3). Therefore, the migration of water was also diminished by the reaction rim.

The reaction rim may have partially dissolved in the second experiment on CVA2 during resaturation with water (see Figure 1). However, the fluid barrier was restored by the formation of a second CaCO₃ layer (see Figures 4f, 5a, and 5b). In other words, even though defects at the reaction front can be introduced when pore water is refreshed (or if other subsurface processes create defects in the CaCO₃ layer), the presence of CO₂ nearly guarantees new blockages. As such, consolidated volcanic ash beds like those in the Campi Flegrei caldera appear inherently equipped to act as barriers to CO₂-rich fluids. These barriers may be intermittent as water or steam circulates within the system, resulting in the repetition of CaCO₃ dissolution and sealing through carbonation. This series of events will contribute to pore pressure fluctuations in the subsurface throughout time. It is worth repeating that further penetration into the central volume of CVA2 was required for the restoration of the fluid seal by way of carbonation. That is, regions containing C-S-H that have already carbonated will not heal via the reactions described by equation (2); they require other chemical/mechanical processes, for example, the crack-seal mechanism (Ramsay, 1980). This means that the cycle of barrier formation through carbonation and barrier breakdown through dissolution or other processes will eventually come to an end if new C-S-H minerals (or other highly reactive metal oxides or silicates) never form. These ideas are collected in Figure 7, which illustrates a few of the competing processes in hydrothermal environments that improve and degrade seals. In the figure we emphasize that pore blockage will be most extreme in hydrous zones (S_w = 100%) where a continuous reaction rim should quickly form to shift CO₂ transport from advective to diffusive. On the contrary, the S_w dependence of the decay rate for permeability during carbonation (see Figure 6) suggests that dry rocks will not act as barriers to gaseous or supercritical CO₂. The key factor seems to be the ratio of the reaction product volumes (CaCO₃ and H₂O) to the pore volume of permeable pathways. Only in extremely tight rocks where C-S-H minerals are adjacent to critical flow paths would the product volumes be sufficient to affect permeability. Our highly porous samples do not satisfy this condition. Hence, sample CVA5c with initial S_w = 12% only experiences a marginal decrease in permeability.
5.3. Structural Integrity of Barriers

Since carbonation leads to pore filling, it is not surprising to find reports of cements that strengthen (Chang & Chen, 2005; Chi et al., 2002; Goñi et al., 2002) or harden (Kutchko et al., 2009) from exposure to high CO2 concentrations and pressures. A notable exception is when cracking during subsequent depressurization cannot be ruled out (Kutchko et al., 2009; Yuanhua et al., 2013). A comparison of Figures 4b–4d verifies that the most damage occurred in the samples that underwent rapid decompression. The fracture pattern is different from the one found by Kutchko et al. (2009) in a pozzolanic Portland cement carbonated with supercritical CO2 (T = 50 °C, Pp = 15 MPa, no confining pressure). However, in both studies fractures along the vertical axis are deduced to be the root cause of the permeability increase. Note that no such defects developed in CVA2 during either slow or rapid depressurization at constant Pc = 10 MPa (see Figure 4b). Its preserved structural integrity indicates that confining pressure can greatly mitigate the damages to a subsurface ash bed (or ash-based cement) that experiences sudden pore depressurization, for example, amidst fault-valve behavior (Sibson, 1990).

Figure 7. Some of the natural processes affecting fluid barriers in hydrothermal systems. There are competing effects that tend to either improve or degrade seals by diminishing or generating permeable pathways. (a) When CO2 enters the pore network of a rock containing reactive minerals the carbonation that ensues fills porosity with carbonate minerals. This constricts flow and, in the case of water vapor-liquid phase boundaries, can produce a continuous carbonate layer that reduces the diffusion rate of CO2 through the pore water. (b) An influx of new water can dissolve carbonate minerals, thereby reopening flow channels. (c) As pore water dries or degasses, local brine becomes supersaturated such that minerals precipitate out of solution and once again fill porosity. (d) Pore pressure buildup from various sources can lead to fractures or the opening of faults. (e) When a water-saturated matrix contains reactive minerals in select regions, those areas seed carbonate formation and thereby slow CO2 transport and block CO2-rich fluid flow. Frames (a)–(c) are presented here as a specific succession of events, but they can occur in any order. Furthermore, the mechanism in (d) can precede or follow any of the others.

5.3. Structural Integrity of Barriers

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Confining pressure can also be argued to have a positive influence on the structural reliability of both Portland cement and our samples as they evolve during carbonation. For instance, in a rare study of carbonation in the presence of confining pressure \( (P_c = 30 \text{ MPa}) \), Liteanu and Spiers (2011) showed that intact plugs exposed to supercritical \( \text{CO}_2 \) \( (T = 80 \, ^\circ \text{C}, \, P_p = 10 \, \text{MPa}) \) followed a clear cut process of densification. In contrast, Fabbri et al. (2009) observed a porous region developing within the reaction front of samples carbonated \( (T = 90 \, ^\circ \text{C}, \, P_p = 28 \, \text{MPa}) \) without confinement, and speculated that this region included a population of microcracks that seeded larger fractures when samples were brought to failure under deviatoric stress. Their proposal is consistent with the microfractures imaged by Li et al. (2015), who inferred a correlation of such defects with a measured decrease in both the modulus of rupture and the elastic modulus after carbonation of unconfined samples. Similarly, Rochelle and Milodowski (2013) observed an enhanced porosity and microfractures ahead of the \( \text{CaCO}_3 \) phase (i.e., in the less carbonated zone) for both cement in laboratory experiments and C-S-H-bearing rocks in nature. However, the cement was unconfined and the rocks were found at (presently) very shallow depths. Our results obtained under \( P_c = 10 \, \text{MPa} \) appear intermediate to the works listed above. We do see a slightly elevated porosity at certain points just beyond the reaction rim (see Figures 4g, 5b, and S3d), probably associated with calcium leaching along the boundary. However, there are no microcracks discernible within this region, that is, no damage was detected near the reaction front that can be directly linked to carbonation. Furthermore, this porous feature does not appear to catalyze fractures during cycles of hydrostatic loading or depressurization. Thus, although deviatoric tests on our samples have not been carried out, we believe that the confining pressure at depth for any ash bed or concrete could be a key factor in preserving its structural integrity during carbonation and rapid changes in pore pressure. In other words, the unsealing mechanism in Figure 7d is probably more relevant to preexisting fractures or faults in and around volcanic ash beds, rather than to any defects that may arise during the carbonation and depressurization of such rocks.

5.4. Applicability to Hydrothermal Systems

Our final remarks pertain to the applicability of this work to actual hydrothermal conditions. Specifically, we consider the physical states of \( \text{CO}_2 \) and water. Taking Campi Flegrei as an example, the temperature of the altered volcanic ash beds of interest, located at depths of 1.5–2.5 km, is in the range of 200–350 °C (De Vivo et al., 1989). These temperatures are clearly supercritical for \( \text{CO}_2 \) (Span & Wagner, 1996); thus, the physical state of \( \text{CO}_2 \) is entirely dependent upon its partial pressure. However, such high temperatures result in physical properties such as density \( (\rho; \, \text{Span} \, \& \, \text{Wagner}, \, 1996) \) and viscosity \( (\mu; \, \text{Fenghour et al.}, \, 1998) \) that are not all that different at depth \( (T = 200–300 \, ^\circ \text{C}, \, P_p = 5–10 \, \text{MPa}, \, \rho = 47–122 \, \text{kg/m}^3, \, \mu = 23.4–28.0 \, \text{mPa} \, \text{s}) \) than in our laboratory \( (T = 33 \, ^\circ \text{C}, \, P_p = 5 \, \text{MPa}, \, \rho = 120 \, \text{kg/m}^3, \, \mu = 16.8 \, \text{mPa} \, \text{s}) \). Moreover, the carbonation of a cement is diffusion controlled both below and above the critical point of \( \text{CO}_2 \) when samples are fully saturated with water because only the dissolved \( \text{CO}_2 \) can react with the matrix (Carey, 2013; Savija & Luković, 2016; Zhang & Bachu, 2011). Therefore, the gaseous \( \text{CO}_2 \) phase used in this work does not invalidate the application of the results to hydrothermal environments.

It remains to be seen how the physical state of water will affect carbonation. For a fluid mixture containing less than 0.1 mole fraction \( \text{CO}_2 \), water is supercritical above approximately 360 °C (Gallagher et al., 1993). Therefore, there is some likelihood that the Campi Flegrei ash beds containing C-S-H minerals are in communication with a \( \text{CO}_2 \)-rich brine, and not a supercritical mixture, at least in the shallowest regions. In those areas we expect \( \text{CaCO}_3 \) barriers to exist or form whenever and wherever \( \text{CO}_2 \) enters the system. If the rock retains a mixture of supercritical water and (gaseous or supercritical) \( \text{CO}_2 \) it is possible that these circumstances are similar to a gaseous mixture of the species, although water would have a higher density. In this case the rock might undergo carbonation comparable to that of CVA in the presence of humidified \( \text{CO}_2 \) gas (i.e., a \( \text{CO}_2\)-\( \text{H}_2\text{O} \) gas mixture), not totally unlike the conditions in the outer regions of our samples.

6. Conclusions

The purpose of this paper has been to investigate the role of \( \text{CO}_2 \) in the destruction or enhancement of permeable pathways throughout volcanic sediments consolidated in the presence of a lime-rich fluid. Volcanic ash was cemented with hydrated lime to produce plugs similar to a low permeability stratum (i.e., caprock) such as that within the Campi Flegrei caldera, but our results are applicable to any metal oxide or...
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Silicate exposed to natural or human-driven carbonating conditions. Gas permeability through the cemented ash was monitored in situ while subjecting each sample to high-pressure CO2. The reaction products, H2O and CaCO3, reduced gas flow through all the plugs. For the two samples with the highest water saturations, the C-S-H within their central volumes was minimally carbonated due to a surrounding rim of CaCO3 that slowed CO2 transport. Although the reaction rim is susceptible to dissolution or cracking, a new barrier will be produced with a fresh flux of CO2 into the system so long as remnant C-S-H is available to be carbonated. Therefore, the geo-material examined here possesses an inherent ability to act as a barrier to CO2-rich fluids. Given that permeability is often assigned a constant value in geophysical models, the changes that we have observed for CVA undergoing carbonation has implications for models that attempt to describe deformation and other phenomena associated with the activity of CO2-rich, hydrothermal fluids in volcanic areas. How the chemical and physical changes concur to affect strength remains to be assessed. As a first step, however, we have observed that the sudden depressurization of CO2 gas only led to a detectable fracture network and permeability increase when samples were unconfined and are thus of primary relevance to near-surface rocks or subsurface locations where significant overpressure resides.
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