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Basalt Reactivity Variability with Reservoir Depth in Supercritical CO₂ and Aqueous Phases

HT Schaef, BP McGrail, and AT Owen

Pacific Northwest Natinoal Laboratory, Richland, Washington, USA

Abstract

Long term storage of CO₂ in geologic formations is currently considered the most attractive option to reduce greenhouse gas emissions while continuing to utilize fossil fuels for energy production. Injected CO_2 is expected to reside as a buoyant water-saturated supercritical fluid in contact with reservoir rock, the caprock system, and related formation waters. As reported by McGrail et al., [1] experiments with basalts demonstrated surprisingly rapid carbonate mineral formation occurring with samples suspended in the supercritical CO₂ (scCO₂) phase. Those experiments were limited to a few temperatures and CO_2 pressures representing relatively shallow (≈ 1 km) reservoir depths. Because continental flood basalts can extend to depths of 5 km or more, in this paper we extend the earlier results across a pressure-temperature range representative of these greater depths. Different basalt samples, including well cuttings from the borehole used in a pilot-scale basalt sequestration project (Eastern Washington, U.S.) and core samples from the Central Atlantic Magmatic Province, were exposed to aqueous solutions in equilibrium with scCO₂ and water-rich scCO₂ at six different pressures and temperatures for select periods of time (30 to 180 days). Conditions corresponding to a shallow injection of CO₂ (7.4 MPa, 34°C) indicate limited reactivity with basalt; surface carbonate precipitates were not easily identified on post-reacted basalt grains. Basalts exposed under identical times appeared increasingly more reacted with simulated depths. Tests conducted at higher pressures (\geq 12 MPa) and temperatures (\geq 55°C), reveal a wide variety of surface precipitates forming in both fluid phases. Under shallow conditions tiny clusters of aragonite needles began forming in the wet $scCO_2$ fluid, whereas in the CO₂ saturated water, cation substituted calcite developed thin radiating coatings. Although these types of coatings were sparse, conditions corresponding to deeper depths showed increasing carbonate precipitation. Basalts exposed to aqueous dissolved CO₂ (25.5 MPa, 116°C) for 30 days were coated in tiny nodules of precipitate (~100 μ m in diameter) that were identified by micro x-ray diffraction as ankerite, [Ca(Fe,Mg)(CO₃)₂], a variety of dolomite commonly associated with hydrothermal and metamorphic environments. Surface characterization by SEM revealed well-developed round nodules composed of discrete individual platelets. In contrast, reaction products forming on the basalt in the corresponding wet $scCO_2$ phase had completely different morphology, appearing in an optical microscope as a surface coating instead of discrete nodules. Examination by SEM revealed layers of discrete platelets forming a cover over a few discrete nodules. Longer test durations (180 days) produced severe iron staining along with minerals structures similar to rhodochrosite and kutnohorite. These preliminary experiments show strong evidence of the faster rate of increase in mineralization reactions taking place in the scCO₂ phase, transformation reactions that are just beginning to be explored in detail.

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Keywords: CO₂; mineralization; carbon sequestration

1. Introduction

Geologic storage of carbon dioxide is expected to allow continued use of fossil fuels while reducing the associated contribution to climate change. Field demonstrations at various stages ranging from initial planning and permitting to injection and post-injection closure activities are exploring the practicability of geologic sequestration [2]. In most cases, dry CO₂ will be injected into reservoirs at depths corresponding to pressure and temperature conditions where CO₂ exists in a supercritical state (>31°C and >10 MPa) [3]. Injected CO₂ is expected to reside as a buoyant water-saturated supercritical fluid in contact with reservoir rock, caprock systems, and related formation waters. Trapping of the CO₂ will be accomplished in three ways: cap rock, dissolution, and mineral trapping. Although mineral trapping via in situ carbonation is not expected to be significant in primary target zones (e.g., siliciclastic sediments with low CO₂ reactivity), it is important in reservoirs containing mafic minerals such as basalts. Laboratory research has shown basalt rocks, rich in Ca²⁺, Mg²⁺, and Fe²⁺ produce carbonate minerals when exposed to aqueous dissolved CO₂ [4-6]. The degree of reactivity between aqueous dissolved CO₂ and different basalts is variable and depends on certain parameters including temperature and pressure.

Until recently, most research was focused on aqueous dominated reactions with little attention given to the wet CO₂ in contact with overlying cap rocks. The reactive nature of this water bearing supercritical fluid is significant and has been shown to produce carbonate minerals when exposed to basalts [1]. Several other researchers have demonstrated the reactivity of water bearing scCO₂, but these were limited in scope and did not address effects of temperature and pressure [7-9]. In this paper we present experimental results of both aqueous dissolved CO_2 and water bearing scCO₂ fluid reactions when exposed to basalt at conditions corresponding to relevant sequestration depths. Basalt formations can extend to depths of 5km or more, resulting in a large range of temperatures and pressures. Solubility of CO_2 in water is weakly dependent on pressure above the critical point and is retrograde with temperature, effects that counter balance. In contrast, water solubility in scCO₂ is a prograde function of temperature and quadruples between 50°C and 100°C at pressures >10 MPa [10]. The increasing amount of water in the scCO₂ phase is expected to influence the rate of precipitation above and beyond what would be predicted to occur from increases in pressure and temperature effects. To examine this effect, well cuttings from a well drilled into the Columbia River Basalt (CRB) as part of the field demonstration site in Wallula, WA (USA) were selected for testing. For comparison, a basalt core representing the Central Atlantic Magmatic Province (CAMP) was also subjected to the same test conditions. The experiments cover a wide range of pressures (7.6 to 31.0 MPa) and temperatures (34° to 136°C) to illustrate impacts of depth on basalt reactivity and carbonation.

2. Method

Well cuttings were selected from the borehole used in a pilotscale basalt sequestration project (Eastern Washington, U.S.). The basalt chips were collected from the Grouse Creek member of the CRB, which was located 1.1 km below the surface. The marble sized cuttings contained visible secondary minerals (heulandite and cristobalite) coating insides of small vesicles. A second basalt sample representing the CAMP was selected from a drill core obtained from the U.S. Geological Survey Test Well DOR-211. This basalt, described in Schaef et al. [4], is without any surface alteration products and is a black, fine grained mafic rock. Preparation of the experiments included photographing the individual basalt chips and describing the obvious alteration



Figure 1. Schematic of experimental setup.

products. High pressure vessels (Parr and Fluitron) were used in these long term static experiments that ran up to 180 days. The vessels (25 or 125 ml) contained pressure transducers and burst discs. Heating of the vessels was accomplished either by heat jackets (Thermotron), ovens (Viking), or quartz sand baths (Boekel). The vessels were loaded by placing three chips into the bottom, covering with water (5-10 ml) and placing three more chips in Teflon baskets suspended in the upper portion of the reactor, well above the water (Figure 1). Each reactor was heated to a pre-determined temperature before using a high pressure syringe pump (ISCO) to add the CO_2 . Pressure and temperature were tracked during the experiments with CO_2 being added if pressure drops were observed. Pressures

and temperatures were selected to be consistent with a standard hydrostatic gradient of 9.8 kPa/m (0.435 psi/ft) and temperature gradient of 45°C/km, respectively.

Table 1.	Experimental conditions	used for high pressur	e testing with basalt	CO2 and precipitate	es identified by
XRD on	post reacted samples afte	r 180 days of testing.			

Reactor	Position ¹	Depth	Pressure	Temp	Color	PPT ²	Phases	
ID	1 OSITION	(m)	(MPa)	(°C)	change	change	(µXRD)	
Central Atlantic Magmatic Province Basalt								
CAMP-1	Т	762	7.5	34	black		NS	
	В	702			black		NS	
CAMP-2	Т	1219	12.0	55	grey	Х	NS	
	В				grey	Х	NS	
CAMP-3	Т	1676	16.5	75	grey	Х	NS	
	В				red	Х	NS	
CAMP-4	Т	2124	21.0	96	red	Х	Aragonite [CaCO ₃] (PDF# 41-1475)	
	В	2134			v red	Х	Calcite [(Ca,Mn,)(CO ₃)] (PDF# 02-0714)	
CAMP-5	Т	2501	25.5	116	v red	Х	Aragonite [CaCO ₃] (PDF# 41-1475)	
	В	2391			v red	Х	Kutnohorite [Ca(Mn,Ca)(CO ₃) ₂] (PDF# 19-0234)	
CAMP-6	Т	20.49	31.0	137	red	Х	Dolomite [CaMgCO ₃] (PDF#11-0078)	
	В	3048			grey	Х	Kutnohorite [Ca(Mn,Ca)(CO ₃) ₂] (PDF# 19-0234)	
Columbia River Basalt								
CRB-1	Т	<u>Т</u> В 762	7.5	34	brown	Х	NS	
	В				brown		NS	
CRB -2	Т	T 1219	12.0	55	grey	Х	NS	
	В				brown	Х	Calcite [(Ca,Mg)(CO ₃)] (PDF#43-0697)	
CDD 2	Т	1676	16.5	75	grey	Х	NS	
CKD-5	В	10/0	10.5		grey	Х	Calcite [(Ca,Mg)(CO ₃)] (PDF#43-0697)	
CPP 4	Т	2134	21.0	96	red	Х	Aragonite [CaCO ₃] (PDF# 41-1475)	
CKD -4	В				red	Х	Calcite [(Ca,Mg)(CO ₃)] (PDF# 43-0697)	
CDD 5	Т	2591	25.5	116	v red	Х	Kutnohorite [Ca(Mn,Ca)(CO ₃) ₂] (PDF# 19-0234)	
CKB-5	В				grey	Х	Calcite [CaMgCO ₃] (PDF# 43-0697)	
CRB -6	T 3048	2049	31.0	137	v red	Х	Rhodochrosite [MnCO ₃] (PDF# 07-0268)	
		3048			grey	Х	Kutnohorite [Ca(Mn,Ca)(CO ₃) ₂] (PDF# 19-0234)	
¹ Denotes sample position within the reactor: $T = top$ (wet scCO ₂) and $B = bottom$ (aqueous dissolved CO ₂)								

² Precipitates detected on surface of reacted grains

NS-not sampled

Once experiments were terminated, reactors were allowed to cool before depressurization. Basalt chips were removed and allowed to air dry. Optical microscopy (National DC5-420T) and scanning electron microscopy (JEOL) with energy dispersive x-ray (SEM-EDX) were used to image surface features including coatings and secondary minerals on unreacted grains, post reacted grains, and polished cross sections of carbonate precipitates. Surface area estimates of carbonate coverage were done based on measurements obtained from the optical microscope. When possible, micro x-ray diffraction (μ XRD) was used to identify precipitates by mounting tiny grains in 0.2-0.6 mm glass capillary tubes (Charles Supper Company). Not all precipitates were of adequate size to be removed and mounted for μ XRD.

3. Results

Experimental conditions, visual observations, and μ XRD results of precipitates removed from reacted basalt are summarized in Table 1. Each reactor contained three basalt chips in the bottom (B) and three more suspended (Teflon basket) in the top (T). Color descriptions are relative and based on the unreacted basalt. Generally, the original basalt colors of grayish brown (CRB) and black (CAMP) transcended into various shades of red. Samples corresponding to shallow depths (CRB-1 and CAMP-1) were visibly unaltered, appearing closest to unreacted basalt. Reaction products on the surface of the basalts became more obvious with increases in temperature and

pressure. Detailed descriptions of reaction products associated with each basalt and test conditions are described below.

CAMP Basalt

Overall, basalts tested at lower pressures and temperatures (CAMP-1, 2, & 3) contained limited carbonate

precipitations. Moderate iron staining appeared at 75°C (16.5 MPa) and became more pronounced with an increase in temperature and pressure (Table 1); negligible color variations were associated with basalts reacted at 34° and 55°C. Reaction products identified on basalts tested at shallow depths (762-1219 m) in the wet scCO₂ (top of reactors) were small (300 μ m) translucent, circular radiating coatings (Figure 2). Chemistries (SEM-EDX) of these precipitates were predominantly Ca, with traces of Fe and Mn. Similar coatings were observed with basalts positioned in the top (T) of reactor CAMP-3, but ~20% larger and containing more cation substitution (Fe, Mn). Additionally, tiny clear elongated crystals, chemically similar to aragonite (CaCO₃), begin to appear on basalts in reactor CAMP-2 (top and bottom).

There is evidence of a high rate of reaction in reactors maintained at 96°C or higher (Table 1). The most notable observation was a presence of orange flakes of Fe (SEM-EDX) on basalts positioned in top and bottom of reactors CAMP-4, 5, & 6. These flakes (~200 µm), also floating freely in the water, were delicate and appeared amorphous when examined by µXRD. In wet scCO₂, carbonates formed as long radiating needles on the basalts at both 96° and 116°C. As shown in Figure 3, these elongated crystals (100 µm) appeared in clusters measuring ~1 mm and were pure Ca (SEM-EDX). Carefully extracted crystals from basalts positioned at the top of CAMP-4 & 5 reactors produced reflections (uXRD) matching aragonite. In contrast, basalts tested at 137°C (T) contained larger precipitates with similar morphologies but a dolomite-ankerite structure (µXRD). Chemistry (SEM-EDX) show these carbonates contain equal amounts of Ca and Fe, consistent with ankerite $[Ca(Ca,Fe)(CO_3)_2]$. Less abundant were transparent radiating coatings, similar to ones described on basalts in



Figure 2. SEM microphotograph of carbonate coating associated with CAMP-1 basalt exposed to wet $scCO_2$ for 180 days (7.5 MPa and 34°C).



Figure 3. SEM microphotograph of aragonite crystals associated with CAMP-4 basalt exposed to wet $scCO_2$ for 180 days (21 MPa and 96°C).

Figure 2 (CAMP-1) were common on basalts removed from the top of reactors CAMP-5 & 6. Although these coatings were dominated by Ca, significant amounts of Fe and Mn were present.

Basalts reacting with aqueous dissolved scCO₂ (B) at 96°C (CAMP-4) contained well developed yellowish to opaque crystals that displayed morphologies completely different than those occurring in the wet scCO₂ fluid. These coatings were identified as a calcite containing Mn (Table 1). Increases in pressure and temperature (CAMP-5 & 6) produced carbonate coatings on the basalts in the aqueous dominated fluid that were large (>1mm), discolored (yellow-red) and more enriched in Mn, Mg, and Fe. Reaction products associated with basalts in CAMP-5 & 6 (B) were identified by μ XRD as kutnohorite, a Mn containing analogue of the dolomite-ankerite series [11].

CRB Basalt

Generally, color changes started occurring at conditions simulating 1676m, and became more pronounced with increasing depth (Table 1). Basalt from CRB-1 and CRB-2 reactors appeared unaltered and contained no obvious precipitations after 180 days of testing. In contrast, basalt from CRB-6 (T) appeared completely coated in a red crust and large white-yellow precipitates.

The first evidence of carbonate precipitation was identified on basalts removed from CRB-2. Examination by SEM revealed tiny ($\sim 20 \ \mu m$) hexagonal crystals with a chemistry dominated by Ca and lesser amounts of Fe and Mn

forming on the surface of basalt reacting with wet scCO₂ (Figure 4). Similar types of coatings were also observed on basalts removed from the bottom of CRB-2. Other types of precipitates, including isolated clusters of radiating crystals were identified basalt removed from CRB-2 (B). Large enough to be extracted for μ XRD, these crystals were identified as Mg substituted calcite. Slightly higher pressures and temperatures produced aragonite, which was observed on the surface of basalt removed from the bottom of CRB-4. This mineral, identified by µXRD, appeared as small colorless radiating crystals. The same basalt exposed to CO₂ dissolved in water (CRB-4) contained vellowish crystals with a fan like crystal habit, often appearing on the chlorites (secondary minerals original present in the unreacted CRB). These crystals were identified as a Mg containing calcite and were identical in structure to crystals forming on the CRB removed from the bottom of reactors CRB-2 & 3.

Similar to the CAMP experiments, the most extensive reaction products were observed on basalts tested at the deepest simulated depths (2591 and 3048m). Basalt from CRB-5 (T) had patches of deep red and contained orange and white crystals identified by uXRD as Kutnohorite. The same basalt removed from the bottom of CRB-5 was coated in discrete carbonate particles (~1mm) identified as Mg rich

This carbonate was also observed at lower calcite [CaMgCO₃]. temperatures and pressures on basalts removed from CRB 2 & 3.

Completely different coatings were observed on basalts removed from CRB-6. Initially, after 30 days of testing, basalts in the bottom of the reactor were coated in tiny nodules of precipitate, measuring ~ 100 um in diameter. Characterization (µXRD) identified these precipitates as ankerite, [Ca(Fe,Mg)(CO₃)₂], a variety of dolomite commonly associated with hydrothermal and metamorphic environments. Surface characterization by SEM revealed well-developed round nodules composed of discrete individual platelets. Chemical composition of these precipitates identified by SEM-EDX is dominated by Ca with minor amounts of Fe, Mg, and Mn. After 180 days of testing, coatings with similar shapes, sizes, and chemistry were observed, but the structure, based on µXRD, changed to kutnohorite.

In contrast, reaction products forming on the basalt in the

corresponding wet scCO₂ phase after 30 days had completely different morphologies, appearing in an optical microscope as a surface coating instead of individual nodules. Examination by SEM revealed layers of discrete platelets forming a cover over a few nodules. Chemistry of appeared these precipitates essentially identical as determined for the samples exposed to the aqueous phase. Following 180 days of testing, a red crust coated the entire basalt surface (CRB-6 T), which was identified by µXRD as having a structure similar to rhodochrosite, a Mn rich carbonate.

(12 MPa and 55°C).

MPa and 137°C).

×100 100Mn

10s870c



ZØKU

Examination by SEM EDX revealed this dense red coating (~25µm thick)





Figure 4. SEM microphotograph of

calcite crystals associated with CRB-2

basalt exposed to wet $scCO_2$ for 180 days

contained twice the amount of Fe compared to Ca and Mg; only traces of Mn were detected. Also observed by SEM were small cylindrical rods forming a mat-like cover on top of the Fe rich carbonate coatings (Figure 5). Chemistry by SEM-EDX indicated this phase was pure silica.

Close examination of vesicles on the basalt removed from the top of CRB-6 showed carbonates formed in and around secondary minerals, most notably chlorite. For example, Figure 6 is a polished cross section of a CRB vesicle filled with chlorite and cristobalite. Present as a red (optical) or bright (SEM) intergrowth within these secondary minerals is the same type of carbonate phase previously identified as kutnohorite. Chemically and structurally these precipitations are identical to coatings formed on the surface of the basalt removed from CRB-6 (T) and represent some of the most extensive carbonate mineral coatings ever observed in such short duration experiments. Overall, the coatings associated with the CRB exposed to wet $scCO_2$ at the highest temperature and pressure, were the thickest and most extensive.

4. Discussion

Two different basalts (CAMP and CRB) were shown to react with aqueous dissolved CO_2 and water saturated scCO₂ to produce carbonates with chemistries, morphologies, and quantities correlated with fluid type and injection conditions (temperature and pressure). A number of researchers have examined the potential of reacting basaltic rocks with aqueous dissolved CO_2 to produce carbonate minerals [2, 5, 12-14]. Carbonates forming as a result of exposing basalts to water equilibrated with scCO₂ were not a surprise; these basalts have been shown to react and produce carbonates in relatively short periods of time [4-5]. However, there is evidence these basalts are less stable with increasing depth, dissolving quicker to release cation-forming carbonates. In the aqueous dominated fluids, more coatings were observed forming on both types of basalt at conditions corresponding to the greatest depths. In these experiments, calcite formed at shallow conditions, indicating the most abundant cation in solution is Ca^{2+} . Increases in depth appear to enhance the concentration of other cations (Fe²⁺, Mg²⁺, and Mn²⁺) favoring the formation of cation substituted calcite and dolomite. This could be an indication certain basalt components such as the pyroxenes are becoming less stable with an increase in depth. On average, Mn is found associated with these pyroxenes, which typically contain between 0.5 to 1.0% oxide wt%. Although the glassy mesostasis is expected to be the fastest dissolving basalt component, it appears the pyroxenes are equally unstable and provide carbonate constitutes such as Mn at greater depths.

On the other hand, reaction products associated with basalts exposed to water rich $scCO_2$ fluids were unique and distinct from ones forming in aqueous based fluids. In some cases complete coatings were observed on these basalts that consisted of Fe rich carbonates with structures similar to dolomite or rhodochrosite. Under SEM, basalt removed from the top of CRB-6 contained a thick ($25\mu m$) carbonate coating that was dominated by Fe-rich species. Also present were cylindrical rods of amorphous Si that formed as a layer on top of the carbonate coating (Figure 5).

Similar carbonate coatings, with an average thickness of 15 μ m, were observed on the CAMP basalt removed from the top of reactor CAMP-6. Although these types of coatings were unique to conditions representing 3048m, there was evidence of similar coatings forming on basalts at 2591m. Mineral reactions in the water rich scCO₂ are not as well understood as the corresponding reactions in water equilibrated with scCO₂. Recent research by Kwak et al. [15] on the reactive nature of wet supercritical fluids has shown forsterite reacts to form magnesite (MgCO₃) under certain conditions (50°C, 100 bar). These authors also report the formation of a highly porous amorphous silica layer.

Temperature conditions for these experiments, 34° to 137° C, correspond to water solubility in the scCO₂ ranging between 1,500 and 20,000 ppmw, respectively [10, 16]. This increase in water content, illustrated in Figure 7 as a function of depth, is significant, with 15



Figure 7. Relative changes of water content in $scCO_2$ as a function of depth (based on standard hydrostatic gradient of 9.8 kPa/m (0.435 psi/ft) and temperature gradient of 45°C/km).

times more water in the scCO₂ at 137°C, than lower temperatures (34°C). In contrast, the amount of CO₂ dissolved into the water changes very little over these depths and temperature intervals. Some minerals, such as portlandite, have been shown to partially react with dry scCO₂ to form carbonates, but completely react in the presence of wet scCO₂ [7-8]. Most recently, work by Loring et al., [17] has shown the reaction between wet scCO₂ and forsterite is related to the amount of water in the system. This work focused on examining reaction rates as a function of available water and the formation of a nanometer thick water layer on the mineral surface at constant pressure (18 MPa) and temperature (50°C). These authors report a correlation between the rate of carbonate formation with the amount of available water and the presence of a thin liquid water film on forsterite particles. These results from these basalt experiments are similar in nature, showing the most severely reacted basalts were exposed to scCO₂ containing the highest amount of water.

One other contributing factor to the overall increase in the rate of carbonation is related to the secondary minerals associated with the CRB. Secondary minerals originally present in the CRB, including chlorite, cristobalite, and heulandite were commonly observed to be associated with higher degrees of carbonation. Samples of CRB tested under moderate conditions contained tiny carbonate precipitates on these secondary minerals, often forming inside the vesicles. Exposing the CRB to the deepest depths appears to have enhanced the formation of carbonates within vesicles lined with chlorite and cristobalite. Large, thin particles of carbonate (> 0.5mm) were easily removed from within these vesicles. Overall, secondary minerals, such as chlorite appear to have enhanced the formation of carbonates, especially when exposed to the water rich $scCO_2$.

5. Conclusion

Two different continental flood basalt samples (CRB and CAMP) were tested under conditions simulating the injection of CO_2 at six different depths. Basalt samples were exposed to either water rich scCO₂ or water equilibrated with scCO₂ for up to 180 days at varying temperature and pressure conditions simulating an injection depth of up to 3048m. Surface coatings on reacted basalt samples became more abundant with an increase in depth, confining the majority of precipitates to conditions $\geq 96^{\circ}$ C and ≥ 21.0 MPa. Reactions in the aqueous dissolved CO_2 generally formed discrete carbonates, featuring either well formed crystals or thin discrete coatings. In contrast, precipitates forming on the basalt as a result of being exposed to wet scCO₂ were comprised of smaller but more abundant crystals, sometimes completely coating the basalt surface. In the most extreme cases Fe-rich carbonate coatings formed a 25 µm thick coating that was subsequently covered in a layer of cylindrical amorphous silica particles. Mineral structures identified by µXRD as occurring in both types of fluid were aragonite, calcite, dolomite, rhodochrosite, and kutnohorite. Cation substitutions within these carbonates were greatest at the higher temperatures and pressures.

Increases in pressure and temperature with depth are well understood to accelerate precipitation reactions in the aqueous phase. However, based on these experiments, the rate of increase appears different depending on whether the reactions take place in the aqueous phase or $scCO_2$ phase. Basalt samples reacted with the wet $scCO_2$ contained the most reaction products including non-carbonate phases relative to samples exposed to the aqueous fluid. At the highest temperatures and pressures basalt samples appeared completely coated in reaction products. These types of transformation reactions are just beginning to be explored in detail, but the dynamics involved will be key elements to understanding basalt-based CO_2 storage

6. References

- 1. McGrail, B.P., et al., *Water reactivity in the liquid and supercritical CO*₂ *phase: has half the story been neglected*?, in *GHGT-9*. 2008: Washington DC.
- 2. Gislason, S.R., et al., *Mineral sequestration of carbon dioxide in basalt: A pre-injection overview of the CarbFix project.* International Journal Of Greenhouse Gas Control, 2010. 4(3): p. 537-545.
- 3. Lin, H., et al., *Experimental evaluation of interactions in supercritical CO₂/water/rock minerals system under geologic CO₂ sequestration conditions.* Journal of Materials Science, 2008. **43**(7): p. 2307-2315.
- 4. Schaef, H.T., B.P. McGrail, and A.T. Owen, *Carbonate mineralization of volcanic province basalts*. International Journal of Greenhouse Gas Control, 2010. 4: p. 249-261.

- 5. McGrail, B.P., et al., *Potential for carbon dioxide sequestration in flood basalts*. Journal of Geophysical Research-Solid Earth, 2006. **111**(B12201): p. ARTN B12201.
- 6. Prasad, P.S.R., et al., *Geological sequestration of carbon dioxide in Deccan basalts: preliminary laboratory study.* Current Science, 2009. **96**(2): p. 288-291.
- 7. Regnault, O., et al., *Experimental study of pure mineral phases/supercritical CO*₂ *reactivity. Implications for geological CO*₂ *sequestration.* Comptes Rendus Geoscience, 2005. **337**(15): p. 1331-1339.
- 8. Regnault, O., V. Lagneau, and H. Schneider, *Experimental measurement of portlandite carbonation kinetics with supercritical CO*₂. Chemical Geology, 2009. **265**(1-2): p. 113-121.
- 9. Busch, A., et al., *Carbon dioxide storage potential of shales*. International Journal Of Greenhouse Gas Control, 2008. **2**(3): p. 297-308.
- 10. Spycher, N., K. Pruess, and J. Ennis-King, CO_2 - H_2O mixtures in the geological sequestration of CO_2 . I. Assessment and calculation of mutual solubilities from 12 to 100°C and up to 600 bar. Geochimica et cosmochimica acta, 2003. **67**(16): p. 3015-3031.
- 11. Bilinski, H., Z. Kwokal, and M. Branica, *Formation of some manganese minerals from ferromanganese factory waste disposed in the Krka River Estuary.* Water Research, 1996. **30**(3): p. 495-500.
- 12. Matter, J.M. and P.B. Kelemen, *Permanent storage of carbon dioxide in geological reservoirs by mineral carbonation*. Nature Geoscience, 2009. **2**(12): p. 837-841.
- 13. Oelkers, E.H., S.R. Gislason, and J. Matter, *Mineral carbonation of CO*₂. Elements, 2008. 4(5): p. 333-337.
- 14. Marini, L., *Geological Sequestration of Carbon Dioxide*. First Edition ed. Developments in Geochemistry. Vol. 11. 2007: Elsevier. 452.
- 15. Kwak, J.H., et al., *Metal carbonation of forsterite in supercritical CO₂ and H₂O using solid state ²⁹Si*, ¹³C, *NMR spectroscopy*. J. Phys. Chem. C, 2010(114): p. 4126-4134.
- 16. Mao, S.D., Z.H. Duan, and W.X. Hu, A vapor-liquid phase equilibrium model for binary CO_2 - H_2O and CH_4 - H_2O systems above 523 K for application to fluid inclusions. Journal of Supercritical Fluids, 2009. **50**(1): p. 13-21.
- 17. Loring, J.S., et al., *Investigation of forsterite carbonation in wet supercritical CO*₂ by in situ infrared spectroscopy: the role of water. Environmental Science & Technology, 2010: p. Submitted.