



## Significance of carbonate buffers in natural waters reacting with supercritical CO<sub>2</sub>: Implications for monitoring, measuring and verification (MMV) of geologic carbon sequestration

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[1] Successful geologic sequestration of carbon in deep saline aquifers requires accurate predictive models of rock-brine-CO<sub>2</sub> interaction. Often overlooked in siliciclastic-hosted saline reservoirs is the carbonate buffering of the groundwater. Carbonate minerals are ubiquitous, even in siliciclastic host rocks, resulting in some carbonate buffering. Geochemical modeling of rock-brine-CO<sub>2</sub> systems often do not accurately predict the geochemical evolution of the system leading to significant doubts in predicting the performance of carbon repositories. New data from a simple NaCl brine-plagioclase hydrothermal experiment tests carbon sequestration in dawsonite and sensitivity to carbonate buffering. This is contrasted to a NaCl brine-siliciclastic rock system containing some initial bicarbonate buffering, analogous to most saline-aquifer sequestration targets, and show that critical errors are caused by incomplete or inaccurate characterization of the *in situ* geochemistry. We provide a methodology that accurately predicts the *in situ* condition using samples collected from brine-rock-CO<sub>2</sub> experiments or well-heads in a carbon sequestration monitoring scenario. **Citation:** Newell, D. L., J. P. Kaszuba, H. S. Viswanathan, R. J. Pawar, and T. Carpenter (2008), Significance of carbonate buffers in natural waters reacting with supercritical CO<sub>2</sub>: Implications for monitoring, measuring and verification (MMV) of geologic carbon sequestration, *Geophys. Res. Lett.*, 35, L23403, doi:10.1029/2008GL035615.

### 1. Introduction

[2] Once supercritical CO<sub>2</sub> is injected into a brine aquifer, what chemical reactions will occur? Will these chemical reactions sequester carbon dioxide either as a dissolved phase or into a neo-formed mineral? And, importantly, can we accurately predict and monitor these processes in a field application? A variety of geochemical processes are implicit in these questions, including dissolution of supercritical CO<sub>2</sub>, formation and dissociation of carbonic acid, and dissolution and re-precipitation of minerals in acidic brine. In order to characterize these processes in the field so that the system can be correctly modeled and monitored, and its performance verified, an accurate characterization of the

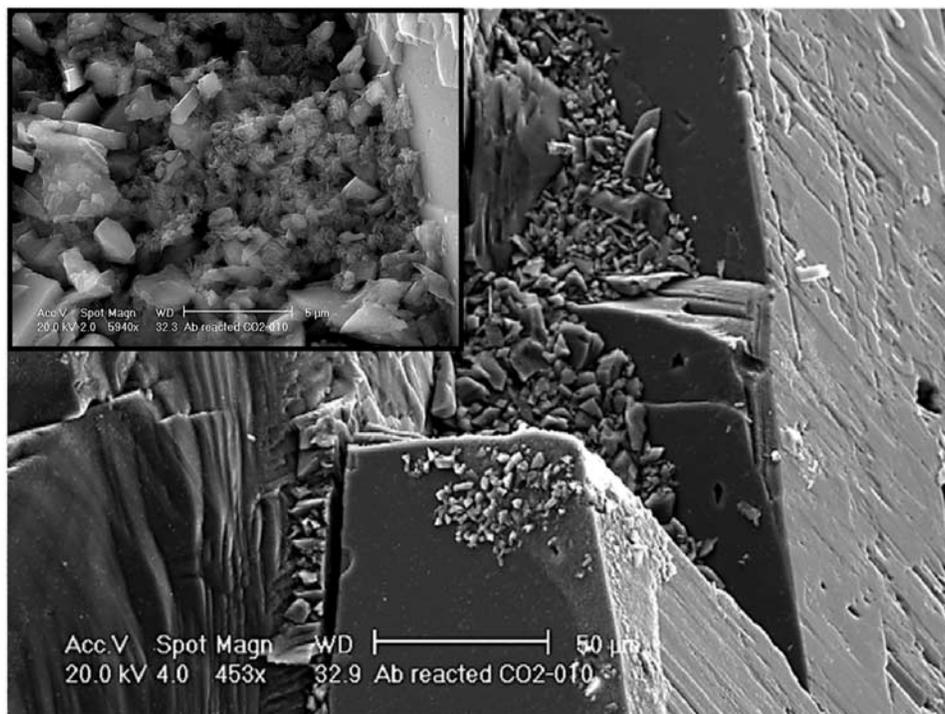
*in situ* aqueous geochemistry is required. *In situ* measurement of geochemistry in CO<sub>2</sub> saturated aqueous systems requires the use of sophisticated devices such as U-tube [Freifeld *et al.*, 2005], Leutert<sup>®</sup> or other similar down-hole samplers [e.g., Goff *et al.*, 1987]. However, routine carbon repository monitoring will require more practical, simpler and less expensive methods that utilize samples collected at the well-head. Thus, computer models are needed to recreate the *in situ* conditions based on surface measurements of fluids that have degassed CO<sub>2</sub>. Reconstructing the *in situ* geochemistry with models based on surface measurements is problematic since the critical parameters are often incorrectly measured or not obtained.

[3] In CO<sub>2</sub>-bearing systems, incomplete characterization of the groundwater requires assumptions about the geochemical system that can lead to incorrect evaluation of rock-water interactions. In particular, without proper characterization of the bicarbonate buffer in saline groundwater, geochemical predictions of rock-water interactions can be woefully inaccurate. Speciation, pH and mineral saturation state predictions, for example, are usually very sensitive to the natural bicarbonate buffer in the water. A 2% error in the bicarbonate content of brines could produce a 1 pH unit error when estimating *in situ* pH, greatly affecting the prediction of mineral saturation indices of carbonate minerals, which is critical for evaluating carbon sequestration in the mineral phase.

[4] Studies directed at understanding the potential of geologic basins for CO<sub>2</sub> storage and the subsequent geochemical behavior of the mixed fluid (CO<sub>2</sub> – H<sub>2</sub>O)-rock system fall into a variety of classes. These include field [Moore *et al.*, 2005], natural analog [Bachu and Bennion, 2007; Carey *et al.*, 2007], modeling [Gunter *et al.*, 2000; Andre *et al.*, 2007], experimental [Druckenmiller and Maroto-Valer, 2005; Lin *et al.*, 2007], and coupled experimental and modeling studies [Shiraki and Dunn, 2000; Kaszuba *et al.*, 2005; Rosenbauer *et al.*, 2005; Suto *et al.*, 2007]. Although these studies advance our understanding, the aqueous geochemistry is incompletely characterized in each. Insufficient data reporting (e.g., incomplete chemistry), inappropriate calculation of *in situ* pH, and incomplete quantification of CO<sub>2</sub> and dissolved inorganic carbon in experiments yield model predictions of mineral precipitation and/or dissolution in conflict with experimental results. For example, Kaszuba *et al.* [2005] observed neo-formed carbonates in run products from supercritical CO<sub>2</sub>-brine-rock experiments, but geochemical modeling predicted carbonates to be undersaturated. Suto *et al.* [2007] reported the opposite phenomenon, predicting carbonate mineral

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**Figure 1.** SEM image showing albite with minor neo-formed aluminosilicate (illite) ( $5 \mu\text{m}$  inset) from the  $75^\circ\text{C}$ , 200 bar, albite + Na-Cl + supercritical  $\text{CO}_2$  experiment. The inset is a magnification of the center of the  $50 \mu\text{m}$  image. Clays are predicted to precipitate, based on geochemical modeling of experimental fluids, in the system prior to  $\text{CO}_2$  injection.

precipitation but not crystallizing carbonates experimentally. Clearly, we must be able to accurately model well-constrained laboratory experiments before we can confidently predict the sequestration of  $\text{CO}_2$  in poorly-constrained natural systems.

[5] Here we present results from a new hydrothermal experiment that emulates a carbon sequestration scenario by injecting supercritical  $\text{CO}_2$  into NaCl brine hosted in a mineralogically simple (mono-mineralic) siliciclastic aquifer. We use an off-the-shelf geochemical code of a type that will be routinely used for carbon repository monitoring to calculate *in situ* conditions and predict mineralization and/or dissolution. We also revisit published experimental results of sequestration in a mineralogically complex (realistic) siliciclastic saline aquifer and recalibrate model predictions and demonstrate the errors stemming from assumptions based on incomplete geochemical analysis. From these two examples we 1) demonstrate the significance of small amounts of carbonate buffer in siliciclastic saline aquifers and 2) identify the key parameters that need to be measured in the fluid chemistry in order to accurately model these systems and develop protocols for reliable Monitoring, Measuring and Verification (MMV) of geologic carbon sequestration.

## 2. Carbon Sequestration in a Saline Aquifer and the Importance of Carbonate Buffer

[6] The brine-rock- $\text{CO}_2$  experiment initially contained NaCl brine, albite and supercritical  $\text{CO}_2$ . No carbonate minerals were present at the start of the experiment and no divalent metal cations that could lead to carbonate mineral precipitation were present in solution (Table 1).

Thus, in addition to evaluating carbonate buffers in a model siliciclastic rock, this experiment tests the reactivity of plagioclase in brine and supercritical  $\text{CO}_2$  and the potential for sequestration of carbon in the mineral dawsonite. Dawsonite,  $\text{NaAl}(\text{CO}_3)(\text{OH})_2$ , is considered a promising phase for the long-term mineral sequestration of  $\text{CO}_2$  in sedimentary basins [Hellevang *et al.*, 2005; Benzeth *et al.*, 2007]. Using established methods [Seyfried *et al.*, 1987; Kaszuba *et al.*, 2005], 1 M NaCl brine and pure albite were reacted for 123 days (2960 hours) at reservoir conditions ( $75^\circ\text{C}$ , 20 MPa) to approach steady state. Supercritical  $\text{CO}_2$  was then injected into the system and the experiment continued for another 45 days (1079 h). Brine was periodically sampled from the ongoing reaction, and solids and quenched brine were analyzed at the conclusion of the experiment (Table 1). Dawsonite was not observed in the post-reaction solids based on SEM imaging and X-ray diffraction analysis of post-reaction solids, while minor illite alteration was observed (Figure 1). Geochemical speciation modeling using The Geochemist's Workbench (GWB) [Bethke, 2006] predicted clay saturation prior to  $\text{CO}_2$  injection, and under-saturation for all minerals (carbonates and silicates) post injection, accurately matching the experimental results. This mono-mineralic example suggests that 1) in the absence of carbonate buffers, brine pH and carbonate mineral saturation evolve independently of fluid-mineral reaction and solely as a function of injected  $\text{CO}_2$  and 2) mineral sequestration in dawsonite is unlikely. Below we contrast these results to an example from the literature that used a more realistic basin mineralogy that shows considerably different behavior based on our recalibrated model results.

**Table 1.** Albite + NaCl Brine + Supercritical CO<sub>2</sub>, 75°C and 200 Bar<sup>a</sup>

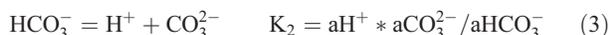
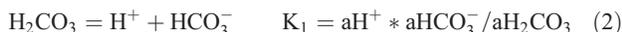
Sample	Hours	Bars	T °C	Al <sup>3+</sup>	Na <sup>+</sup>	SiO <sub>2</sub> (aq)	HCO <sub>3</sub> <sup>-</sup>	CO <sub>2</sub> Total	Cl <sup>-</sup>	SO <sub>4</sub> <sup>2-</sup>	Ca <sup>2+</sup>	Fe <sup>2+</sup>	K <sup>+</sup>	Mg <sup>2+</sup>	pH Bench	pH <i>In Situ</i> <sup>b</sup>
start	0.0	1	21	0.01	23614	0.75	1.8	1.8	35626	19.7	0.0	0.0	0.0	0.0	7.99	7.99
1	9050.9	194	75	0.14	23934	9.57	6.0	6.0	39238	26.6	0.0	0.0	0.0	0.0	8.95	8.21
2	626.8	191	75	0.19	23906	9.89	5.4	5.4	35654	1.80	26.4	0.07	12.8	2.33	7.65	7.25
3	1128.8	199	74	0.11	24213	10.37	5.2	5.2	35311	2.18	12.1	0.02	11.0	2.31	7.31	7.05
4	2953.5	202	76	0.12	21245	9.85	17.0	17.0	36442	8.15	10.8	0.05	6.21	0.63	6.31	6.35
5	2976.8	350	76	3.54	20730	35.42	nd <sup>c</sup>	41866	36145	8.44	36.3	8.10	10.3	1.46	4.80	3.11
6	3096.9	335	75	4.90	20874	35.55	nd <sup>c</sup>	nd	36417	0.20	53.8	0.93	11.7	1.32	4.57	nd
7	4944.6	330	75	5.05	21309	44.70	nd <sup>c</sup>	58325	36069	5.02	9.12	3.75	14.6	0.86	4.63	3.04

<sup>a</sup>All concentrations in ppm; nd, not determined.

<sup>b</sup>*In situ* pH calculated using The Geochemist Workbench by reacting degassed fluid chemistry from 25 to 75°C and then titrating in the CO<sub>2</sub> total less the dissolved HCO<sub>3</sub><sup>-</sup> (~17 ppm).

<sup>c</sup>CO<sub>2</sub> injected after sample -04; HCO<sub>3</sub><sup>-</sup> not determined on post injection samples - only total system CO<sub>2</sub>; the pre-inject value of 17 ppm HCO<sub>3</sub><sup>-</sup> is assumed; The water rock ratio at the start of the experiment was 118:1. We injected 15.4 grams of CO<sub>2</sub> with water: rock ratio at 77:1 after sample -04.

[7] A critical error propagated in the literature that leads to disparity between modeling and experimental results is not completely defining pH, dissolved inorganic carbon, and/or quantity of supercritical CO<sub>2</sub> injected into the geochemical system. The interdependence of these parameters and the importance for accurately determining each is evident by considering the equations governing aqueous carbonate speciation and pH control. Dissolved CO<sub>2</sub> in fluid systems exists as H<sub>2</sub>CO<sub>3</sub>, HCO<sub>3</sub><sup>-</sup> and CO<sub>3</sub><sup>2-</sup>, and the activity of these species in solution and the pH of that solution are a function of one another. The speciation of dissolved inorganic carbon can be described by the well known reactions and associated equilibrium expression (equations (1)–(3)):



Thus, the total dissolved inorganic carbon in solution can be expressed as:

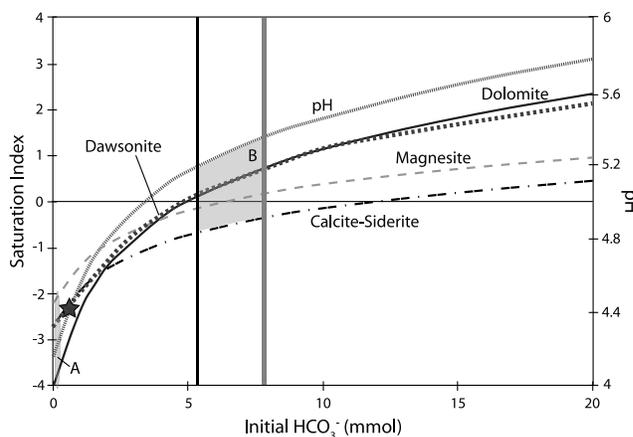
$$\sum \text{CO}_2(\text{aq}) = \text{H}_2\text{CO}_3 + \text{HCO}_3^- + \text{CO}_3^{2-} \quad (4)$$

By substituting between equilibrium expressions, an equation that describes the pH of a solution is:

$$\text{pH} = \text{p}K_1 + \log(a\text{HCO}_3^- / a\text{H}_2\text{CO}_3) \quad (5)$$

where  $\text{pH} = -\log(a\text{H}^+)$  and  $\text{p}K = -\log(K)$ . Built into this equation is the impact of temperature ( $\text{p}K$  varies with temperature) and the buffering affect of bicarbonate on solution pH.

[8] These parameters are extremely difficult to measure within supercritical CO<sub>2</sub>-brine-rock laboratory experiments that emulate sedimentary basin pressures and temperatures. This problem is analogous to the difficulty of collecting *in situ* fluids from monitoring wells. Fluid samples withdrawn from experiments cool and degas CO<sub>2</sub>, processes which drastically alter pH. For example, *Kaszuba et al.* [2005] report degassed brine chemistry, including measured pH,



**Figure 2.** Dawsonite SI sensitivity based on a 1 molal NaCl brine + albite + supercritical CO<sub>2</sub>(1325 mmolal) experiment (75°C, 200 bar). The initial bicarbonate in this simple system is constrained by equilibrium with atmospheric CO<sub>2</sub>, and dawsonite is undersaturated (star). Also shown is calcite, siderite, magnesite and dolomite saturation index and pH sensitivity to dissolved HCO<sub>3</sub> concentration based on *Kaszuba et al.* [2005]. Experimental conditions were 5.5 molal NaCl brine + argillaceous shale, 270 mmolal total CO<sub>2</sub>, 200°C, and 200 bars. To explore sensitivity, the initial bicarbonate content was varied from near-zero to 20 mmolal-aqueous CO<sub>2</sub> was added using GWB, while preserving a total CO<sub>2</sub> of 270 mmolal. For example, at 10 mmolal HCO<sub>3</sub>, 260 mmolal CO<sub>2</sub>(aq) is added. Predicted SI's by *Kaszuba et al.* [2005] are represented by box A, with an initial HCO<sub>3</sub> content constrained by equilibrium with atmospheric CO<sub>2</sub>. We propose more realistic SI's within grey area (box B), based on a lower initial HCO<sub>3</sub>(black bar) constrained by the pre-CO<sub>2</sub> injection total system CO<sub>2</sub> reported by *Kaszuba et al.* [2005], and an upper limit (grey bar) based on forward modeling using GWB (see text for details). Dawsonite solubility in our experiment shows a similar sensitivity initial bicarbonate concentration exemplifying the importance of the bicarbonate buffer. Saturation Index (SI) =  $\log(\text{IAP}/K_{\text{sp}})$  for the mineral in question, where IAP is the ion activity product and  $K_{\text{sp}}$  is the solubility product. A SI > 0 indicates super saturation, a SI < 0 indicates under saturation, and SI = 0 implies equilibrium.

major ion chemistry and total *in situ* CO<sub>2</sub>. The dissolved carbonate species (HCO<sub>3</sub><sup>-</sup> and CO<sub>3</sub><sup>2-</sup>) were not measured, but CO<sub>3</sub><sup>2-</sup> can be ignored because at pH < 9 it exists in insignificant amounts [Drever, 1997]. The authors used these data with GWB to add CO<sub>2</sub> into a bicarbonate free solution and calculate *in situ* pH and mineral saturation indices (SI) (pH ≈ 4.4 and carbonate mineral SI ≪ 0, see Figure 2, box A). Their omission of the initial bicarbonate concentration in the modeling resulted in predictions that did not agree with experimental products. Figure 2 illustrates the sensitivity of carbonate mineral SI and fluid pH to the initial quantity of bicarbonate in solution. We revise the Kaszuba *et al.* [2005] *in situ* chemistry calculations and mineral saturation index predictions by estimating the amount of bicarbonate buffering in solution two ways. First we assume the bicarbonate in solution is the pre-CO<sub>2</sub> injection total CO<sub>2</sub> (~5 mmolal) as determined from sampling and analysis of experimental fluids. This estimate is a minimum because the authors did not measure dissolved carbonate species after CO<sub>2</sub> injection, and the solution may have acquired additional buffering due to subsequent mineral-fluid interaction. Forward modeling of their rock-brine-CO<sub>2</sub> experiment using GWB was used to estimate this additional buffering and suggests that ~8 mmol of dissolved HCO<sub>3</sub><sup>-</sup> should be in solution and accounted for during mineral saturation index calculation. Forward modeling was conducted by first reacting (equilibrating) the starting mineralogy and brine chemistry reported by Kaszuba *et al.* [2005] at 200°C, followed by titrating in the amount of CO<sub>2</sub> injected in their experiment. This estimate is considered a maximum since the geochemical model assumes equilibrium is reached. Both the lower and upper estimates are adequate to increase *in situ* pH by approximately 0.5 pH units, pushing calcite and siderite to near equilibrium (SI = 0) and dolomite and magnesite to supersaturation (SI > 0) (Figure 2, box B). These revised estimates are consistent with the precipitation of early magnesite and later reaction to siderite reported by Kaszuba *et al.* [2005]. While this concentration of bicarbonate is small compared to the total system CO<sub>2</sub> (2–3% of the total), the disconnect between modeling predictions (no carbonate precipitation) and experimental results (neo-formed carbonate) hinges on this subtle difference. The presence of a small amount of bicarbonate buffer must be explicitly accounted for in computational models.

[9] Again, our mono-mineralic experiment shows that dawsonite is undersaturated at the experimental conditions (Figure 2). The initial dissolved carbonate in this experiment was quite small, controlled by solution equilibration with atmospheric CO<sub>2</sub> prior to sealing the experiment. However, Figure 2 indicates that the solubility of dawsonite is sensitive to the initial bicarbonate content, and that only ~5 mmol initial bicarbonate is needed to push dawsonite to saturated conditions. The difference between our experiment and that of Kaszuba *et al.* [2005] is that our experiment is a very simple system of one pure silicate (albite) containing a mono-valent metal cation and the latter replicated a realistic siliciclastic host rock containing a complex mineralogy that provided divalent metal cations and small but significant bicarbonate buffering during rock-water-CO<sub>2</sub> reaction. If our experiment had contained a more realistic starting mineralogy including other silicate minerals and/or

a small amount of carbonate mineral, the solution would have acquired some bicarbonate buffering and achieved conditions favorable for dawsonite precipitation. Most siliciclastic sedimentary formations are not mono-mineralic and small amounts of carbonate minerals, as detrital grains and as secondary cements, are common, and based on this study, are important for initial carbonate buffering, subsequent rock-brine interaction and mineralization after CO<sub>2</sub> injection.

### 3. Implications for MMV of Carbon Sequestration

[10] Accurate and complete characterization of the aqueous chemistry in siliciclastic saline reservoirs targeted and utilized for geologic sequestration of CO<sub>2</sub> is critical for reliable predictions and measurements of performance. A commonly overlooked problem in saline reservoirs is the sensitivity in geochemical model predictions of pH evolution, mineralization and dissolution to carbonate buffering in groundwater. Even in these saline systems, dissolved carbonate is present in solution because of the ubiquitous presence of some carbonate minerals and cements in the majority of siliciclastic rocks. Based on the examples presented in the previous sections, we have shown the importance of considering geologically realistic scenarios. Also, to accurately construct geochemical models for prediction, evaluation of experiments and evaluation of actual field applications, the following parameters must be accurately measured or calculated: 1) major and minor ion chemistry 2) dissolved carbonate species concentration (i.e., HCO<sub>3</sub><sup>-</sup> and CO<sub>3</sub><sup>2-</sup>), 3) total dissolved CO<sub>2</sub> and 4) *in situ* pH. Because water samples will cool and degas CO<sub>2</sub>, with associated changes in pH, during extractions from experiments or wells, it is difficult to determine the *in situ* pH and dissolved carbonate distribution. By measuring the total amount of CO<sub>2</sub> (by capturing water and gas quantitatively) and measuring the pH and dissolved carbonate in degassed samples, *in situ* geochemical conditions (pH and bicarbonate buffering) can be accurately calculated. Using this method, we have shown that reliable predictions of mineralization and dissolution, critical for the successful application of geological CO<sub>2</sub> sequestration, are possible with off-the-shelf geochemical modeling software. In terms of large scale sequestration efforts and routine MMV, this approach is attractive because samples can be collected at the surface from nearly any monitoring well, providing an inexpensive and relatively simple alternative and/or addition to *in situ* sample collection and analysis using sophisticated and expensive down-hole devices.

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