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Supercritical carbon dioxide and sulfur in the Madison Limestone: A natural analog in southwest Wyoming for geologic carbon–sulfur co-sequestration

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ABSTRACT

The Madison Limestone on the Moxa Arch, southwest Wyoming, USA contains large volumes (65–95%) of supercritical CO_2 that it has stored naturally for 50 million years. This reservoir also contains supercritical H_2S , aqueous sulfur complexes (SO_2^{4-} and HS^{-}), and sulfur-bearing minerals (anhydrite and pyrite). Although SO_2 is not present, these sulfur-bearing phases are known products of SO_2 disproportionation in other water–rock systems. The natural co-occurrence of SO_4^{2-} , S^{2-} , supercritical CO_2 and brine affords the opportunity to evaluate the fate of a carbon–sulfur co-sequestration scenario.

Mineralogic data was obtained from drill core and aqueous geochemical data from wells outside and within the current supercritical CO₂-sulfur-brine-rock system. In addition to dolomite, calcite, and accessory sulfurbearing minerals, the Madison Limestone contains accessory quartz and the aluminum-bearing minerals feldspar, illite, and analcime. Dawsonite (NaAlCO₃(OH)₂), predicted as an important carbon sink in sequestration modeling studies, is not present. After confirming equilibrium conditions for the Madison Limestone system, reaction path models were constructed with initial conditions based on data from outside the reservoir. Addition of supercritical CO₂ to the Madison Limestone was simulated and the results compared to data from inside the reservoir. The model accurately predicts the observed mineralogy and captures the fundamental changes expected in a Madison Limestone-brine system into which CO₂ is added. pH decreases from 5.7 to 4.5 at 90 °C and to 4.0 at 110 °C, as expected from dissolution of supercritical CO₂, creation of carbonic acid, and buffering by the carbonate rock. The calculated redox potential increases by 0.1 V at 90 °C and 0.15 V at 110 °C due to equilibrium among CO₂, anhydrite, and pyrite. Final calculated Eh and pH match conditions for the co-existing sulfur phases present in produced waters and core from within the reservoir. Total dissolved solids increase with reaction progress, mostly due to dissolution of calcite with an accompanying increase in dissolved bicarbonate. The Madison Limestone is a natural example of the thermodynamic end point that similar fluid-rock systems will develop following emplacement of a supercritical CO2-sulfur mixture and is a natural analog for geologic carbon-sulfur co-sequestration.

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1. Introduction

Geologic sequestration of CO_2 generated by coal-fired power plants is a critical component of Carbon Capture and Storage (CCS) (Pacala and Socolow, 2004). In addition to CO_2 , coal combustion generates SO_x , NO_x , and other constituents (Thambimuthu et al., 2005). Purity requirements for CO_2 injected into a geologic reservoir

* Corresponding author: Tel.: +1 307 766 6065; fax: +1 307 766 766 6679. *E-mail addresses*: John.Kaszuba@uwyo.edu (J.P. Kaszuba), asitchle@mines.edu are being debated worldwide and have yet to be established (Gale, 2009). Conventional CO_2 separation technologies (e.g., methyl ethanolamine absorption and stripping) that can be retrofitted to existing power plants yield CO_2 that is greater than 90% pure (Rao and Rubin, 2002). However, these technologies impose large parasitic energy costs of 30 to 40% of the net power plant output. In addition, even just a few tenths of a percent of the common impurities (e.g., SO_x and NO_x) will influence the geochemistry of a water–rock system. Novel technologies such as oxy-fuel combustion and integrated gasification combined cycle (IGCC) power plants dramatically reduce parasitic energy costs but also produce higher levels of impurities in the combustion products (Apps, 2006). In either case, any industrial process is susceptible to off–normal occurrences and accidents that may inadvertently introduce impurities into the CO_2 that is injected into the geologic storage reservoir. Geologic sequestration of CO_2 that

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contains impurities is known as co-sequestration, a term first used with reference to co-injected CO_2 and H_2S (Williams, 2002). The geochemical effects of co-injected impurities on a geologic storage reservoir and its caprock are largely unknown. Research efforts must address whether the geochemical behavior of these impurities can be integrated with separation strategies to optimize disposal of co-injected combustion gasses.

Natural accumulations of CO_2 in the crust provide analogs to geologic formations that will become artificially charged with anthropogenic CO_2 (Allis et al., 2001). These natural analogs have stored CO_2 for geologically significant time and provide a means of understanding and predicting how CO_2 will behave in a carbon repository. Initial studies of natural analogs focused on the Colorado Plateau and the Southern Rocky Mountains, including Bravo Dome in New Mexico, McElmo Dome and Sheep Mountain in Colorado, Farnham Dome in Utah, and the Springerville–St. Johns field in Arizona and New Mexico (Allis et al., 2001; Gilfillan et al., 2008, 2009; Moore et al., 2005; Pearce et al., 1996; Stevens et al., 2001). Natural gas fields containing significant amounts of CO_2 (28 to 50 mol%) have also been studied as natural analogs (Lu et al., 2009; Wilkinson et al., 2009).

The Mississippian Madison Limestone on the Moxa Arch of southwest Wyoming, USA is recognized as a natural analog for geologic carbon sequestration (Allis et al., 2001). The Madison Limestone as well as several other Paleozoic units on the Moxa Arch contains natural accumulations of supercritical CO₂, including the Bighorn Dolomite, Tensleep Sandstone, and Phosphoria Formation (De Bruin, 1991), thus the Moxa Arch houses multiple natural analogs to geologic carbon sequestration. In addition to supercritical CO₂, the Madison Limestone contains sulfur in multiple oxidation states, including SO_4^{2-} in anhydrite and formation waters, S^{2-} in pyrite and as H₂S gas, and S° in native sulfur. While SO₂ was not introduced into the Madison Limestone, these sulfur-bearing phases are known products of SO₂ reaction in other water-rock systems (Getahun et al., 1996; Holland, 1965; Symonds et al., 2001). The natural cooccurrence of aqueous and mineral SO_4^{2-} , S^{2-} , and S° with supercritical CO₂ and brine in the Madison Limestone affords the opportunity to evaluate the fate of a carbon-sulfur co-sequestration scenario.

In this paper we present mineralogic data obtained from drill core and aqueous geochemical data from wells that penetrate the Madison Limestone on the Moxa Arch, both within and proximate to the margins of the existing supercritical CO₂ reservoir. We use these data to constrain geochemical reactions within the Madison Limestone supercritical CO₂-sulfur-brine-rock system, especially reactions among the sulfur- and aluminum-bearing accessory minerals that are present. Geochemical reactions among these accessory minerals and coexisting fluids serve to elucidate multiphase fluid $(CO_2 + H_2O)$ rock interactions in a carbonate-dominated system. We construct a geochemical model of this system based on the mineralogy and aqueous geochemistry, validate the model against published aqueous data using stability diagrams, and illustrate the geochemical consequences of emplacement of supercritical CO₂ into the brine-rock system using an Eh-pH diagram. The model suggests that the Madison Limestone fluid-rock system is at thermodynamic equilibrium and provides insight into the geochemical behavior of CO₂ and sulfur that naturally reside in the Madison Limestone on the Moxa Arch. Understanding this natural supercritical CO₂-sulfur-brine-rock system helps clarify potential long-term storage behavior of reactive CO2 and sulfur in a carbonate reservoir and demonstrates the utility of the Madison Limestone as a natural analog for carbon-sulfur cosequestration. Our analysis also provides insight into fluid-rock interactions that take place during acid gas storage in carbonate reservoirs. To our knowledge, this is the first description in the scientific literature of a suitable natural analog for carbon-sulfur co-sequestration.

2. SO₂ reactions in water-rock systems

The essential problem facing geologic co-sequestration of a CO_2 -SO₂ mixture is that SO₂, the most abundant constituent in SO_x, is very reactive in water-rock systems. Several aqueous reactions have been discussed in the literature, including hydrolysis of SO₂ to produce sulfurous acid, a weak acid (Ellis et al., 2010):

$$SO_2 + H_2O \Leftrightarrow H_2SO_3$$
 (1)

Reaction (1) can only proceed if no geochemical redox reactions involving SO_2 take place. Under strongly oxidizing conditions SO_2 reacts to produce sulfuric acid, a strong acid (e.g., Ellis et al., 2010):

$$SO_2 + H_2O + \frac{1}{2}O_2 \iff H_2SO_4$$
(2)

 SO_2 can also react with steam to produce sulfuric acid and hydrogen gas, but this reaction is limited to the gas phase (Symonds et al., 2001):

$$SO_2 + 2H_2O \Leftrightarrow H_2 + H_2SO_4$$
 (3)

 SO_2 reacts in water–rock systems to form native sulfur and sulfuric acid by undergoing a disproportionation reaction (Holland, 1965):

$$3SO_2 + 2H_2O \Longleftrightarrow S + 2H_2SO_4 \tag{4}$$

Finally, SO₂ also reacts in water–rock systems to form sulfuric acid and hydrogen sulfide, a weak acid, by a different disproportionation reaction (Getahun et al., 1996; Holland, 1965; Symonds et al., 2001):

$$4SO_2 + 4H_2O \Longleftrightarrow 3H_2SO_4 + H_2S \tag{5}$$

Disproportionation of SO₂ to form sulfuric acid and aqueous hydrogen sulfide is the predominant reaction in a variety of waterrock systems spanning a wide range of geochemical conditions (Getahun et al., 1996; Holland, 1965; Symonds et al., 2001), including the geochemical conditions of the Madison Limestone. SO₂ disproportionation to form sulfuric acid and hydrogen sulfide is also believed to be the predominant reaction for SO₂ in geologic carbon sequestration scenarios (Palandri and Kharaka, 2005; Palandri et al., 2005; Xu et al., 2007). Once formed, subsequent dissociation of sulfuric acid and aqueous hydrogen sulfide generates acidity. Significant changes to pH, the master variable of aqueous systems, perturb a wide range of water-rock reactions and processes and transform the manner in which the geochemistry of the system ultimately evolves.

Several types of fluid injection and disposal operations are somewhat comparable to large-scale CO₂-SO₂ co-sequestration. For roughly 20 years, the oil and gas industry has disposed of H₂S by injection of CO₂-H₂S mixtures into the subsurface (Bennion and Bachu, 2008; Chakma, 1997). An H₂S–CO₂ mixture, or acid gas, is the byproduct of the process of "sweetening" hydrocarbons that contain H₂S (Machel, 2005). Interest in CCS has spawned a new industrial paradigm coupling acid gas disposal to geologic carbon sequestration (Bennion and Bachu, 2008; Gunter et al., 2000; Machel, 2005). Within this paradigm, laboratory experiments have been performed to evaluate the effects of CO₂-H₂S mixtures on the relative permeability of reservoir rocks (Bennion and Bachu, 2008) and the geochemistry of wellbore cements (Jacquemet et al., 2005, 2008; Pironon et al., 2007). Experimental constraints restricted the latter to elevated temperatures and pressures (200 °C and 50 MPa) from which the authors extrapolated to reservoir conditions. A recently completed field experiment injected 35,000 tons of a 70% CO₂-30% H₂S mixture into a carbonate oil reservoir, the Zama oilfield, in Alberta, Canada (US Department of Energy, 2010).

The practice of deep well injection of acidic liquids into geologic formations is also well established. Acid injection in hydrocarbon production is a known technique to stimulate reservoir permeability (e.g., Hendrickson et al., 1992), and H_2SO_4 -bearing waste has been disposed by injection into subsurface carbonate formations (e.g., de Graaff, 1998). Finally, CO_2 - H_2S co-injection is planned for waste gas produced by the Hellisheidi geothermal power plant in southwest Iceland (Gislason et al., 2010).

Most published research focuses on computational approaches to CO_2 -SO₂ co-sequestration. Most of these modeling studies predict that CO_2 -SO₂ co-sequestration will produce highly reactive waterrock systems (Gunter et al., 2000; Knauss et al., 2005; Palandri and Kharaka, 2005; Xu et al., 2007). The predicted range of outcomes includes: 1) extreme acidity (to pH 1 precluding carbonate precipitation); 2) iron reduction and subsequent siderite precipitation; 3) precipitation of sulfate minerals as a sulfur trapping mechanism; 4) significant development of mineral alteration zones near points of injection; and 5) redistribution of porosity between mineral alteration zones and reservoir margins. In contrast, two modeling studies predict that CO_2 -SO₂ co-sequestration will not yield highly reactive water-rock systems because SO₂ will not readily diffuse out of the co-injected supercritical CO_2 and into coexisting brine (Crandell et al., 2010; Ellis et al., 2010).

Only two relevant experimental studies have been published. One evaluates the potential for SO₂ to reduce Fe³⁺ to Fe²⁺ and promote siderite precipitation (Palandri et al., 2005). The second suggests that small amounts of SO₂ (<1 mol%) do not interfere with CO₂ sequestration, as compared to baseline CO₂ sequestration experiments without SO₂ (Nogueira and Mamora, 2008).

Our understanding of the geochemical behavior of SO₂ relative to geologic carbon sequestration is obviously limited. Assumptions and conflicting model predictions regarding SO₂ reactivity require testing and evaluation in natural as well as experimental systems, especially because multiphase fluid (CO₂–H₂O)–rock processes are exceedingly complex and often defy standard geochemical expectations (Kaszuba et al., 2003, 2005). For example, processes coupled to the reactivity and acidity of a multiphase fluid–rock system, such as mobilization and re-precipitation of silica, could armor and protect flow paths or plug them (Kaszuba and Janecky, 2009; Kaszuba et al., 2005).

3. Geologic setting of southwest Wyoming

The Moxa Arch is a 200 km long, north-south trending Cretaceous anticlinal uplift (Kraig et al., 1987) located in southwestern Wyoming (Fig. 1). It is bound on the west by the Laramide Overthrust Belt and on the east by the Rock Springs Uplift. In an area of approximately 1200 km² along northern portion of the Arch, several thousand feet of Paleozoic section, including the Mississippian Madison Limestone, contains CO₂ (between 65 and 95 vol.%), CH₄ (up to 22%), N₂ (up to 7%), H₂S (up to 4.5%), and He (up to 0.5%) (De Bruin, 1991). These rocks are at depths greater than 2000 m, thus temperatures and pressures exceed the critical points of CO₂ (30.98 °C, 7.38 MPa), CH₄ $(-82.7 \degree C, 4.596 \text{ MPa})$, and H₂S (100 $\degree C, 8.937 \text{ MPa})$, and these fluids occur in the supercritical state. Gas from two small Madison Limestone fields located on the northern end of the Moxa Arch produces helium for industrial use and CO₂ for enhanced oil recovery in Wyoming and Colorado. Data from Madison Limestone drill core along the northern portion of the Moxa Arch show gas saturation values ranging from only a few percent to as high as 90% of the pore space (Wyoming Oil and Gas Conversation Commission, 2010). The timing of CO_2 emplacement is poorly constrained. CO_2 was probably emplaced 50 million years ago in association with mantle-derived magmatic sources (Huang et al., 2007). No supporting evidence is available for this age (Huang et al., 2007) and no other published literature evaluates the age of CO₂ emplacement. The volume of CO₂ has been estimated at 114 trillion cubic feet (tcf) $(3.23 \times 10^{12} \text{ m}^3 \text{ or})$ approximately 5.9×10^9 metric tons) in the Madison Limestone and



Fig. 1. A) Generalized geologic map of southwestern Wyoming, USA. Trace of the crest of the Moxa Arch and location of wells where Madison Limestone drill core was sampled are plotted. The extent of the supercritical CO_2 reservoir is based on the work of Stilwell (1989), although uncertainties exist for the subsurface disposition of supercritical CO_2 (De Bruin, 1991). B) Stratigraphic correlation of major units within Madison Limestone adapted from Katz et al. (2007) and Thyne et al. (2010). Dashed lines indicate unconformities. Locations of core samples collected for this study (stars) are illustrated.

240 tcf (6.80×10^{12} m³ or approximately 8.6×10^{9} metric tons) within the entire Paleozoic section (De Bruin, 1991).

4. Methods and approach

A limited number of drill cores and water analyses exist for the Madison Limestone on the Moxa Arch. Nonetheless, enough of these data are available to provide background data from outside the existing supercritical CO₂ reservoir as well as data from a well within the reservoir. Data from within the reservoir constrain the endpoint of supercritical CO₂-sulfur-brine-rock interactions and help to validate geochemical models of co-sequestration. Samples of Madison Limestone from the Moxa Arch were collected from drill core available at the Core Research Center of the U.S. Geological Survey (US Geological Survey, 2010). Three wells defining a broad transect outside the existing reservoir and one well within the reservoir were chosen for study. The Chevron Federal 1-29 and Union Pacific RR #4 are located on the western and eastern margins of the Arch, respectively, whereas the Church Buttes #31 is located on the southern crest of the Arch (Fig. 1). The Riley Ridge 33-24 is located on the northern end of the Arch within the reservoir. Four samples from different depths within each of the four wells were evaluated (Fig. 1, Table 1).

Mineralogy and petrology of the sixteen samples were determined using X-ray diffraction (XRD), scanning electron microscopy (SEM), and standard petrographic thin section techniques. Samples for whole rock XRD analysis were ground and sieved to 325 mesh (less than 45 µm diameter) and analyzed from 2° to 70° 2θ using a SCINTAG XDS2000 powder diffractometer. Once whole rock XRD analysis was completed, ground samples for the Chevron Federal 1-29, Church Buttes #31, and Union Pacific RR #4 wells were prepared for clay analysis. Each of these samples was suspended in a deflocculant (Calgon) by sonification and subsequently permitted to settle for approximately 2.5 h. Clay fractions (less than 2 µm diameter) were separated from the rock powder by decanting the liquid. An oriented clay mount was prepared from the decanted material using vacuum filtration. Oriented clay samples were analyzed from 2° to 35° 2θ.

Available analyses of Madison Limestone formation waters were compiled from the USGS Produced Waters Database (Breit and Skinner, 2002) and the Wyoming Oil and Gas Conservation Commission website (Wyoming Oil and Gas Conversation Commission, 2010). The quality of these data was evaluated using charge and mass balance criteria. Samples exceeding \pm 10% charge or mass balance

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Sample depth meters (feet)	Carbonate minerals ^a	Silicate minerals ^b	Sulfur-bearing minerals ^c		
Wells located outside t	he supercritical CO ₂ 1	reservoir			
Chevron Federal 1-29					
4511 (14,801)	Do, Ca	N.O.	An		
4514 (14,810)	Do, Ca	Qz, It	N.O.		
4735 (15,534)	Do	Ac	N.O.		
4740 (15,552)	Do	Qz, It	An		
Church Buttes #31					
5590 (18,340)	Do, Ca	N.O.	An, Py ^d		
5606 (18,394)	Do	N.O.	Ру		
5691 (18,670)	Ca	Qz	An ^d		
5702 (18,706)	Do	Ac	An, Py ^d		
Union Pacific RR #4					
2288 (7505)	Do, Ca	Qz, It	Py ^d		
2313 (7588)	Do	Ac	An ^d		
2368 (7769)	Do	N.O. ^e	An, S, Py ^d		
2390 (7843)	Do	Fs, Qz, It	An ^d , Py ^d		
Well located within the	e supercritical CO ₂ re	servoir			

Kiley Kluge 55-24			
4732 (15,526)	Do, Ca	Qz	An
4738 (15,544)	Do, Ca	Qz	N.O.
4854 (15,924)	Do, Ca	Qz	N.O.
4862 (15,953)	Do, Ca	Qz	An

^a Do = dolomite, Ca = calcite.

^b Qz = quartz, It = illite, Ac = analcime, Fs = feldspar.

^c Py = pyrite, An = anhydrite, S = native sulfur.

were excluded from consideration, resulting in a total of 14 acceptable water analyses (Table 2). All values in Table 2 are listed as reported in the primary literature except temperature and potassium. *In-situ* temperature was calculated for each sample by comparing sample depth and regional geothermal gradient (22.4 °C/km, 6.8 °F/1000 feet). Potassium analyses were not reported for several samples. For these samples we estimated potassium concentrations based on Na:K ratios of the other samples. Water analyses were speciated using Geochemist's Workbench (GWB) version 8 (Bethke and Yeakel, 2009) to calculate ion activities for plotting on stability diagrams, which were also made using GWB and constrained by the formation water chemistry.

Our strategy is to first demonstrate the system is at thermodynamic equilibrium by plotting the water chemistry on the appropriate stability diagrams. We then construct reaction path models for the addition of supercritical CO₂ to the brine-rock system using the actual mineralogy and aqueous geochemistry of the Madison Limestone as constraints. The results from the reaction path model are compared to the mineralogy from the well located within the reservoir. For this investigation we assumed equilibrium rather than use a kinetic model because temperatures are elevated in the Madison Limestone (Table 2), fluid-rock reaction rates are fast relative to the long residence time of CO₂ (Huang et al., 2007), and our initial speciation calculations showed the aluminum-bearing minerals were at equilibrium with pore water in the Madison Limestone. Our use of an equilibrium model also permits us to evaluate the efficacy of equilibrium models for evaluating long-term storage behavior of reactive carbon and sulfur. In contrast, simulations of sequestration injection scenarios will require kinetic models since the primary interest will be on short-term reactions and CO₂ mobility.

Numerical simulations were performed using GWB (Bethke and Yeakel, 2009), the database thermo.com.v8.r6+.dat and the B-dot ion association model. Given that the salinity of some of the solutions is greater than 75,000 ppm, the preferred activity formulation is ionpair. However, databases for the ion-pair formulations (Pitzer, Harvie-Møller-Weare) do not have sufficient data to use in this system. The partitioning constant of CO₂ into water that is resident in GWB was adjusted according to the equation of state of Duan et al. (2006) for seawater at 90 and 110 °C and 38 MPa. Since none of the brine analyses reported silica, iron, or aluminum concentrations, values consistent with quartz equilibrium for silica, pyrite equilibrium for iron and 10 parts per billion (ppb) total aluminum were assumed as initial values. Quartz and pyrite are present in the Madison Limestone (Table 1), and 10 ppb aluminum represents near equilibrium with primary feldspars. An initial value for dissolved silica, iron, and aluminum that is near mineral equilibrium allows numeric stability during the reaction path calculation. The resulting model is relatively insensitive to the initial values since the system is also constrained by equilibrium with the mineral assemblage present in the Madison Limestone (dolomite, calcite, anhydrite, pyrite, quartz, and illite, Table 1). Minerals not present in the Madison Limestone are suppressed from participating in reaction path calculations.

5. Results

5.1. Mineralogy and petrography

The Madison Limestone on the Moxa Arch is a dolostone due to widespread early dolomitization (Budai et al., 1987). Euhedral dolomite (Fig. 2) is the only carbonate mineral identified in seven of the samples and the predominant carbonate mineral, relative to calcite, in another eight samples (Table 1). Calcite occurs mostly as secondary cement within pores and fractures in these eight samples. Calcite is the only carbonate mineral identified in one sample from drill core, the Church Buttes #31 on southern the crest of the Arch at a depth of 5691 m (Fig. 1, Table 1). These observations are consistent with the known Madison Limestone stratigraphy in the area, which is

^d Mineral not identified by X-ray diffraction but observed in thin section. ^e N.O. = none observed.

Table 2

Madison Limestone formation water chemistry.

Well name (API#)	Location	Date sampled	Depth meters (feet)	pН	T (°C) [†]	TDS (calc)	Na ⁺	K ⁺	Ca ²⁺	${\rm Mg}^{2+}$	HCO ₃ ⁻	Cl-	SO_4^{2-}	Charge balance (%)
17 M (4901305634)	T33N R96W	8/2/57	3400	6.1	93	16,203	585	53	3074	1522	256	10,400	310	1.1
Unit 17 M (4901305634)	S15 T33N R96W	8/15/64	(11,155) 3354 (11,002)	7.7	92	17,329	802	10.3	3100	1630	314	10,900	521	0.0
Unit 32 M (4901305652)	T33N R96W	8/15/64	(11,002) 3416 (11,205)	7.3	93	22,098	512	11.3	4210	2270	251	14,500	308	0.0
34 M (4901305702)	T33N R96W S10	9/28/55	3479	7.0	94	31,507	8329	761	2508	601	245	18,500	535	3.8
Unit No.1 (4902905822)	T53N R100W S27	6/22/49	3342 (10.961)	7.4	91	17,284	3173	290	2249	231	3150	6360	1839	1.7
Unit No. 1 (4902905822)	T54N R100W S21	12/16/51	4739 (15,545)	7.8	123	16,860	4676	427	939	91	1610	5800	3259	2.9
Teepee Mtn. Unit #1 (4903720754)	T12N R104W S17	6/6/72	4829 (15,840)	6.9	125	79,486	27,700	1890	864	398	2680	44,200	1830	0.6
Unit 22-19 (4903505746)	T28N R113W S19	N.D.	4182 (13,718)	7.9	110	29,727	9000	823	250	101	5290	3940	10,300	4.6
Champlin #549 (4904120145)	T17N R116W S3	3/21/74	2966 (9730)	7.5	83	24,904	8220	752	545	134	1190	11,400	2650	4.9
ACG #2 (4904120117)	T17N R119W S18	8/6/74	4018 (13,180)	6.7	107	22,465	3140	614	3430	651	1280	10,500	2870	0.9
5 Amoco Chevron Gulf (4904120268)	T17N R119W S18	9/2/83	4073 (13,360)	6.1	108	7948	2720	248	180	18.9	205	4510	58.8	4.2
1-A Champlin 457 Amoco B (4904120265)	T18N R119W S31	5/21/8	3916 (12,844)	6.5	104	156,821	42,300	3860	10,300	4000	1710	94,000	719	4.3
Snow Hollow #1 (4902320226)	T24N R120W S35	8/18/73	3171 (10,400)	8.2	88	12,228	3520	98.8	605	60.7	364	3810	3710	0.0
1 Champlin 323 Amoco B (04904120265)	T31N R119W S31	5/21/80	4396 (14,420)	8.8	115	39,491	11,800	1080	2290	666	200	22,800	173	9.0

All solutes in mg kg⁻¹ as reported except some potassium values that were estimated as described in the text. Value at top of sample interval given in table. [†]Temperatures calculated from depth and geothermal gradient (22.4 °C/km, surface T = 16.2 °C). pH values are reported. N.D. = no data.

N.D. = 110 data.

composed of thick intervals of dolomitized limestone interbedded with thin limestone intervals and primary and secondary anhydrite (Thyne et al., 2010). Interiors of dolomite grains in many samples are cloudy when viewed under plane polarized light whereas the edges are clear due to the presence or absence of fine-grained inclusions, respectively. Alternating bands of Fe-rich and Fe-poor dolomite are observed on grain margins, suggesting mineral recrystallization and a complicated fluid history.

In addition to dolomite and calcite, the Madison Limestone contains sulfur- and aluminum-bearing accessory minerals. Secondary anhydrite occurs in at least two samples from each of the drill cores (Table 1) as optically-continuous pore-filling precipitates and as secondary fracture fill (Fig. 2). Recrystallized interstitial pyrite occurs in the Church Buttes #31 and Union Pacific RR #4 drill cores (Table 1, Fig. 3). Native sulfur fills pores between euhedral dolomite crystals in one sample, the Union Pacific RR #4 at the 2368 m interval (Fig. 4).

Accessory quartz, feldspar, analcime, and illite are present in the Madison Limestone (Table 1). Interstitial quartz (Fig. 2B) and chert cement occur in about half of the samples from each of the four drill cores. Small feldspar peaks are observed in XRD data for one sample of drill core, the Union Pacific RR #4 at the 2391 m interval. Analcime was identified optically and by XRD analysis in one sample from each of the three drill cores outside the reservoir (Table 1, Fig. 2D). It occurs as euhedral grains interstitial to dolomite crystals in samples that contain no quartz. Illite is the only clay mineral identified by XRD analysis. It occurs in half of the samples from the Chevron Federal 1-29 and Union Pacific RR #4 drill cores.

5.2. Geochemical modeling

Mineral stability diagrams that depict the activity of sodium versus silica and potassium versus silica are presented in Figs. 5 and 6, respectively. Stability fields are plotted at both 90 and 110 °C,

temperatures bracketing those found in the Madison Limestone. Also plotted in Figs. 5 and 6 are analyses of formation waters presented in Table 2. Formation water samples are from locations within and outside the supercritical CO_2 reservoir. The samples plot within, or on, phase boundaries for the predicted stability fields for muscovite (illite proxy), albite, K-feldspar and analcime. This predicted mineral assemblage compares well with the actual aluminum-bearing mineral assemblage observed in drill core samples (Table 1). This supports the interpretation that formation water is in equilibrium with the minerals in the Madison Limestone. The presence of analcime in the Madison Limestone and in our geochemical models is also consistent with analcime crystallization in experiments (Kaszuba et al., 2005).

The next step is to formulate reaction path models that simulate emplacement of supercritical CO₂ into the Madison Limestone. Our conceptual model assumes that Madison Limestone outside the supercritical CO₂ reservoir on the Moxa Arch represents formation conditions prior to CO₂ emplacement. Thus we choose as a starting fluid composition a representative water analysis from a well outside, but at a similar depth to, the reservoir (Champlin #549, Table 2). The initial mineral assemblage in the model is dolomite, calcite, anhydrite, pyrite, illite, and quartz, identical to the observed mineralogy. Dawsonite was suppressed since none was observed in the core samples or has ever been reported in the study area (Budai et al., 1984, 1987). Total dissolved sulfur content is controlled by equilibrium with anhydrite, the phase with the greatest mass of sulfur. Since the timing of CO₂ emplacement is poorly constrained but is post burial, we construct models at temperatures bracketing current burial conditions (90 and 110 °C) and pressure equivalent to 3660 m (38 MPa), which represents an intermediate depth among the drill core samples (see Table 1). On an Eh-pH diagram, the composition of the aqueous solution at these initial conditions plots on the phase boundary between the pyrite and anhydrite stability fields (Fig. 7). The presence of native sulfur in one sample outside the reservoir (Table 1) suggests



Fig. 2. A through C) Photomicrographs of Madison Limestone in Chevron Federal 1-29 at a depth of 4740 m. A and B) Optically continuous, poikilitic secondary anhydrite (Anh) fills pores among euhedral dolomite (Do) rhombohedrons. A small amount of interstitial quartz (Qtz) is pictured in B. Illite was identified by XRD analysis but is not pictured in these views. Scale bar is 600 µm in A and 500 µm in B. C) Secondary anhydrite fills a fracture that cuts the dolomite matrix. Scale bar is 2 mm. D) Photomicrograph of Madison Limestone in Church Buttes #31 at a depth of 5702 m. Secondary anhydrite fills pores among euhedral dolomite rhombohedrons. Euhedral analcime (Ac) is also present within the pores. Pyrite is present in this interval of drill core but is not pictured in this view. Scale bar is 500 µm.



Fig. 3. Images of pyrite in Madison Limestone from Church Buttes #31 at depth of 5590 m. A) SEM micrograph of recrystallized secondary pyrite (light gray) fills pores between dolomite (dark gray). Scale bar is 600 µm. B) Reflected light image of the same view. Pyrite is bright colored, dolomite is gray in color, and pores are black.



Fig. 4. Secondary electron SEM micrographs of native sulfur in Madison Limestone from the Union Pacific RR #4 well at a depth of 2368 m. Secondary native sulfur (lighter mineral labeled S) fills pores between surrounding euhedral dolomite (darker mineral labeled Do). Scale bars are 200 µm.

that conditions during native sulfur precipitation were more acidic or possessed higher total dissolved sulfur, or both.

CO₂ gas is subsequently added to this ideal Madison Limestone-fluid system until final CO₂ (aq) reaches a value of about 1.2 m, equivalent to equilibrium with supercritical CO₂ at 3660 m and 38 MPa (Duan et al., 2006). Addition of CO₂ establishes a reaction path along the anhydrite– pyrite phase boundary such that pH decreases and Eh increases (Fig. 7). End points of reaction paths for 90 °C and 110 °C correspond to the start and end of arrows depicted in Fig. 7. pH decreases from 5.7 to 4.5 at 90 °C and to 4.0 at 110 °C due to dissolution of CO₂ into the brine and the resulting dissociation of carbonic acid, together with reaction with the mineral assemblage. An Eh increase of approximately 0.1 V at 90 °C and 0.15 V at 110 °C accompanies addition of CO₂ and the concomitant pH decrease. The endpoint of this reaction path approaches the junction of the stability fields of pyrite, anhydrite, native sulfur, and H_2S (Fig. 7). The endpoint is dependent on the final fugacity of CO₂, which is a function of depth assuming free phase supercritical CO₂ in equilibrium with the hydrostatic gradient. CO₂ could be at higher pressure if the system is over-pressured. Higher CO₂ pressures will not significantly decrease pH since the increase in dissolved CO₂ (aq) with increasing pressure and temperature is small above the conditions modeled (Duan et al., 2006).

The simulation captures the fundamental changes expected in a Madison Limestone-brine system into which CO_2 is added. The simulation predicts the well-known pH decrease that accompanies addition of CO_2 to a water–rock system (Fig. 7). The magnitude of the predicted decrease, roughly 1.2 pH units, is consistent with experimental (Kaszuba et al., 2003, 2005) and computational (Gunter et al.,



17M Unit 17M Unit 32M K-feldspar 34M 8 Unit No. 1 I Champlin #549 Δ Snow Hollow No. 1 ☆ 7 Unit 22-19 Δ \diamond ACG No. 2 log activity K⁺/H⁺ 5 Amoco Chevron Gulf X 6 1-A Champlin 457 Amoco B 0 Muscovite 1 Champlin 323 Amoco B 5 Gibbsite Kaolinite 0 -4 -3 -2 -5 log activity SiO₂(aq)

Fig. 5. Log activity Na⁺/H⁺ versus log activity SiO₂(aq) diagram for brine analyses for Madison Limestone from Table 2 at 90 °C (solid lines) and 110 °C (dashed lines), temperatures observed in portions of the Madison Limestone. All samples are from outside the supercritical CO₂ reservoir except Unit 22-19. This predicted silicate mineral assemblage (phyllosilicate \pm feldspar \pm analcime) for the Madison Limestone-multiphase fluid (CO₂ + H₂O)-system agrees well with the observed assemblage, indicating that formation brines are in equilibrium with the host formation.

Fig. 6. Log activity K⁺/H⁺ versus log activity SiO₂(aq) diagram for brine analyses for Madison Limestone from Table 2 at 90 °C (solid lines) and 110 °C (dashed lines), temperatures observed in portions of the Madison Limestone. All samples are from outside the supercritical CO₂ reservoir except Unit 22-19. This predicted silicate mineral assemblage (phyllosilicate \pm feldspar) for the Madison Limestone-multiphase fluid (CO₂ + H₂O)-system agrees well with the observed assemblage, indicating that formation brines are in equilibrium with the host formation.



Fig. 7. Eh–pH diagram showing stability of sulfur phases at 90 °C (solid lines) and 110 °C (dashed lines). Early burial and diagenesis of Madison Limestone precedes reaction paths for addition of CO_2 at 90 °C and 110 °C. End points of these two reaction paths correspond to ends of arrows and approach equilibrium with pyrite, native sulfur, anhydrite, and H₂S(g), phases which are all present in the Madison Limestone. The exact endpoint of each reaction path depends on the fugacity of CO_2 , which is related to depth assuming free phase supercritical CO_2 .

2000) studies as well as with field studies of enhanced oil recovery (Bowker and Shuler, 1991) and pilot-scale sequestration projects (Kharaka et al., 2006) in siliciclastic reservoirs. *In-situ* pH data is not available for the Madison Limestone on the Moxa Arch. To our knowledge, *in-situ* pH has only been calculated, not measured, for carbonate reservoirs hosting enhanced oil recovery or pilot-scale sequestration projects. The Weyburn Oil Field, for example, is a carbonate reservoir that has been the site of both enhanced oil recovery and carbon sequestration. *In-situ* pH values of 6.8 to 6.9 and 5.1 to 5.3 are calculated for pre- and post-CO₂ emplacement, respectively (Cantucci et al., 2009). This calculated pH decrease (up to 1.8 pH units) compares favorably with values calculated in this study.

As the calculated pH decreases, small amounts of calcite dissolve and anhydrite precipitate. Iron carbonate (siderite) is not stable under these acidic conditions. Total dissolved solids (TDS) increase with reaction progress to 77,000 mg kg⁻¹, mostly due to dissolution of calcite with an accompanying increase in dissolved bicarbonate. Preliminary models that included addition of SO₂ in amounts expected in co-sequestration (Section 6) produce the same end products with only very small differences in pH and Eh evolution.

The simulation accurately predicts mineral assemblages that are observed in the well located inside the reservoir (Riley Ridge 33-24). The endpoint of the reaction path in the Eh–pH diagram is on the pyrite–anhydrite boundary, which is the mineral assemblage observed in the reservoir (Fig. 7, Table 1). In addition, the overall change in mineral volumes is very small. This finding is in agreement with prior studies of petrophysical properties of the Madison Limestone in the study area that show no significant difference in porosity for samples within and outside of the reservoir (Thyne et al., 2010).

To further evaluate the system, we simulated the production of fluid from 90 °C and 38 MPa to surface temperature and pressure. As pressure is reduced the dissolved CO₂ decreases, as does dissolved bicarbonate, and pH increases as a consequence of cooling and depressurization of the fluid. Calcite precipitates and yields water at surface conditions with a TDS value of 24,103 mg kg⁻¹. TDS values observed in formation water samples produced from the reservoir on the Moxa Arch (Tip Top Field, unit #22-19, Table 2) are 28,660 mg kg⁻¹, uncorrected for changes during production. Thus the composition of the final aqueous solution calculated by the model is both reasonable and very similar to water produced from the reservoir of the Moxa Arch.

6. Carbon and sulfur in the Madison Limestone

Supercritical CO₂ and multiple phases of sulfur (aqueous SO₄²⁻ and HS⁻, supercritical H₂S, anhydrite and pyrite) are present inside the existing Madison Limestone reservoir of the Moxa Arch. The mineralogy and aqueous geochemistry of this brine–rock system offer endpoints in the likely reaction path of SO₂ disproportionation and provide insight for the fate of sulfur during co-sequestration. This portion of the Madison Limestone thus serves as an analog for long-term storage conditions for geologic co-sequestration of reactive carbon and sulfur.

Several modeling studies predict crystallization of dawsonite, NaAlCO₃(OH)₂, in carbon repositories (Johnson et al., 2001; Knauss et al., 2005; Xu et al., 2004, 2007; Zerai et al., 2006) and enhanced oil recovery projects (Cantucci et al., 2009). However, dawsonite is rarely observed in natural analogs (Klusman, 2003; Moore et al., 2005; Pearce et al., 1996; Wilkinson et al., 2009) and does not form in laboratory experiments that emulate a carbon repository (Hangx and Spiers, 2009; Kaszuba et al., 2003, 2005; Newell et al., 2008; Pearce et al., 1996). Consequently, the importance of dawsonite to CCS is the subject of ongoing debate (Bénézeth et al., 2007; Hellevang et al., 2005, 2011; Kaszuba et al., 2011; Wilkinson et al., 2009). XRD, SEM, and petrographic analysis revealed no dawsonite in the Madison Limestone, nor has any been reported in previous studies of this formation (Budai et al., 1984, 1987). Instead, aluminum-bearing minerals in the Madison Limestone are analcime, feldspar, and illite whereas carbonate minerals are limited to dolomite and calcite. For these reasons we suppressed dawsonite in our models (Section 5.2). If not suppressed, the models predict that dawsonite will precipitate. This discrepancy supports the growing recognition that computer simulations do not accurately portray dawsonite precipitation in natural systems. Our results suggest that dawsonite will not be an important carbon sink for long-term geologic carbon sequestration in carbonate reservoirs that contain accessory aluminum-bearing minerals.

In the geochemical model, Eh increased as CO_2 was added. Final Eh–pH conditions place the solution near the junction of the stability fields of pyrite, anhydrite, native sulfur, and H_2S (Fig. 7) suggesting that Eh may be controlled by equilibrium among the sulfur species. SO_2 disproportionation to sulfuric acid and hydrogen sulfide takes place in a variety of water–rock systems and is proposed as the predominant SO_2 reaction in geologic carbon sequestration scenarios (Palandri and Kharaka, 2005; Palandri et al., 2005; Xu et al., 2007). This is not to suggest that SO_2 was naturally introduced into the Madison Limestone, only that both SO_4^{2-} and S^{2-} , the products of SO_2 disproportionation, are naturally present in the Madison Limestone. Geochemical modeling of CO_2 – SO_2 co-injection into a water–rock system predicts alunite, anhydrite, and pyrite precipitation (Xu et al., 2007). With the exception of alunite, these sulfur-bearing minerals are also present in the Madison Limestone.

To evaluate how a carbon–sulfur co-sequestration scenario might actually evolve in a carbonate reservoir we modified the reaction path model by adding 100 ppm SO₂ and repeated the calculations. In this revised calculation, SO₂ reacts according to Eq. (5) and produces a reaction path that coincides with the reaction path plotted in Fig. 7. This revised model predicts SO₂ disproportionation leading to the same mineral assemblage and fluid chemistry as observed in the Madison Limestone on the Moxa Arch, reinforcing our conclusion that the Madison Limestone can serve as a natural analog to geologic carbon-sulfur co-sequestration.

Identifying the source or sources for CO_2 and H_2S in the Madison Limestone on the Moxa Arch is beyond the scope of this study. CO_2 in fields on the Colorado Plateau and in the Southern Rocky Mountains, including Bravo Dome in New Mexico, McElmo Dome and Sheep Mountain in Colorado, Farnham Dome in Utah, and the Springerville– St. Johns field in Arizona and New Mexico, is derived from mantle sources as determined by noble gas isotopes (Gilfillan et al., 2008). CO_2 on the Moxa Arch is also believed to be derived from mantle sources (Huang et al., 2007), although definitive geochemical data have yet to be published. H_2S is generated by a variety of natural processes that include thermogenic sulfate reduction and methaneanhydrite reactions (Cross et al., 2004; Machel et al., 1995). The intriguing possibility for the Madison Limestone is that supercritical CO_2 emplacement drove Eh-pH reactions and enhanced sulfate reduction to produce both methane and native sulfur.

Geochemical reactions among sulfur- and aluminum-bearing accessory minerals in the Madison Limestone on the Moxa Arch elucidate multiphase fluid $(CO_2 + H_2O)$ -rock interactions and provide insight into the behavior of CO₂ and sulfur that naturally reside in a carbonate-dominated system. Understanding this supercritical CO₂sulfur-brine-rock system provides insight into long-term storage behavior of reactive CO₂ and sulfur in a carbonate reservoir and also provides important constraints on laboratory experiments and computer simulations. Long-term storage behavior is the last of several stages in the life cycle of a carbon repository (Benson and Cook, 2005). Dynamic processes that accompany initial CO₂ injection, such as hydrodynamic flow and kinetic reactions, are beyond the scope of this paper but represent fruitful areas of future research. Identifying short term reactions in reservoirs and caprocks and determining the potential importance of metastable phases and intermediate reaction steps are critically important to understanding the short-term fate of sulfur introduced with CO₂, particularly for developing accurate risk assessments. Theoretical calculations (Crandell et al., 2010; Ellis et al., 2010) suggest that release of co-injected SO₂ from within the supercritical CO₂ phase and into formation brine will be diffusion-limited. Will SO₂ be mobile and reactive or will SO₂ persist within supercritical CO₂ because of limited diffusivity? Detailed petrographic and isotopic studies of the Madison Limestone and other formations on the Moxa Arch as well as relevant laboratory experiments are needed to address these questions.

7. Conclusions

A relatively simple equilibrium model of the Madison Limestone was constructed using mineralogic data and published water analyses to describe reactions among supercritical CO₂, Madison Limestone, and resident formation water. The model makes accurate predictions for crystallization of sulfur- and aluminum-bearing accessory minerals and captures the fundamental changes expected in a Madison Limestone-brine system into which CO₂ is added. The following are concluded:

- The Madison Limestone-fluid system appears to be in thermodynamic equilibrium as determined by mineralogy and aqueous geochemistry of formation brines.
- 2) CO₂ was introduced into portions of the Madison Limestone and has been stored naturally for approximately 50 million years (Huang et al., 2007). Adding CO₂ to the model Madison Limestone-brine system decreases pH and increases both Eh and TDS. The endpoint of the reaction path on the Eh–pH diagram is on the pyrite–anhydrite boundary, which is the mineral assemblage observed in the reservoir. Eh may be controlled by equilibrium among CO₂ and the sulfur-bearing phases. The modeling results show that properly formulated and constrained equilibrium

models can be useful for predicting the long-term fate of reactive carbon and sulfur in a co-sequestration scenario.

- 3) Multiple sulfur phases (aqueous SO₄²⁻ and HS⁻, supercritical H₂S, recrystallized anhydrite and pyrite) predicted by the model and observed in the natural CO₂-brine-rock system offer thermody-namic endpoints in likely reaction paths and are a good indication of the fate of sulfur during carbon-sulfur co-sequestration.
- 4) In addition to dolomite, calcite, and accessory sulfur-bearing minerals, the Madison Limestone contains accessory quartz and the aluminum-bearing minerals feldspar, illite, and analcime. No dawsonite, NaAlCO₃(OH)₂, is observed. Although dawsonite is an important carbon sink in numerous sequestration modeling studies, the mineralogy of the Madison Limestone suggests that dawsonite will not be important to geologic carbon sequestration in carbonate reservoirs that contain accessory aluminum-bearing minerals.
- 5) Geochemical reactions among sulfur- and aluminum-bearing accessory minerals in the Madison Limestone on the Moxa Arch elucidate multiphase fluid $(CO_2 + H_2O)$ -rock interactions and provide insight into the behavior of CO_2 and sulfur that naturally reside in a carbonate-dominated reservoir. Thus the Madison Limestone on the Moxa Arch serves as a natural analog for long-term geologic co-sequestration of reactive carbon and sulfur.

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