Isotopic Analysis of Sulfur Cycling and Gypsum Vein Formation in a Natural CO₂ Reservoir

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Abstract

In order to assess the long-term security of geologic carbon storage, it is crucial to study the geochemical behavior of sulfur in reservoirs that store CO₂. Fossil fuel combustion may produce mixtures of carbon dioxide and sulfur gases, and the geochemical effects of sulfur-CO₂ cosequestration are poorly understood. This study examines sulfur mineralization from a core drilled in a stacked sequence of natural CO₂ reservoirs near the town of Green River, Utah. These reservoirs include the Entrada and Navajo Sandstone, which are separated by the Carmel Formation caprock, and are transected by a system of CO₂-degassing normal faults, through which saline CO₂-charged brines discharge. Our objective in this study is to evaluate the mechanisms and timing of secondary mineral formation, particularly gypsum formation, in the CO₂ reservoirs and intervening caprock. The Carmel Formation contains beds of gypsum within a fault zone. Secondary veins of gypsum exist throughout the Entrada Sandstone and Carmel Formation. We report sulfur and oxygen isotope data ($\delta^{34}\text{S}_{\text{SO}_4}$ and $\delta^{18}\text{O}_{\text{SO}_4}$, respectively) measured in gypsum and $\delta^{34}\text{S}$ in pyrite, and the oxygen and hydrogen isotope composition ($\delta^{18}\text{O}$ and δD , respectively) of gypsum hydration water. The multiple isotope approach allows us to trace the sources of sulfur in the reservoirs and, when combined with structural and petrological evidence, the progress of fluid-rock reactions and relative timing of vein mineralization.

The secondary gypsum veins in the Carmel Formation derive from mixing of fluids with two isotopically distinct sulfate sources: sulfate from the gypsum beds within the Carmel Formation and sulfate-rich brines that originate from evaporites in the underlying Carboniferous Paradox Formation. The gypsum veins in the Entrada Sandstone have a relatively wide range of $\delta^{18}\text{O}_{\text{SO}_4}$, both isotopically more enriched in ^{18}O and more depleted in ^{18}O than the primary gypsum sources. We suggest that

some aqueous sulfate in the Entrada Sandstone may cycle through multiple valence states as it undergoes reduction and reoxidation, resulting in the replacement of its oxygen atoms and allowing the occasional formation of gypsum with anomalous low $\delta^{18}\text{O}_{\text{SO}_4}$. Our data from gypsum hydration water indicates that groups of gypsum veins formed at two different times. Gypsum veins in the Entrada Sandstone and some of the veins in the Carmel Formation likely formed during Quaternary CO₂-charged brine discharge events, while other veins located close to the gypsum beds in the Carmel Formation formed earlier, likely during cycles of dehydration and rehydration associated with the Laramide-age (40 Mya) faulting. We conclude that calcium-sulfate mineral formation in brine-filled fractures may play an important role in inhibiting fluid migration in geologic reservoirs that contain CO₂.

1.1 Introduction

Predicting the security of geologic CO₂ storage sites requires an understanding of the geochemical behavior of the stored CO₂ (Moore et al., 2005; Balashov et al., 2013). A factor that may affect this geochemical behavior is the presence of dissolved sulfur or sulfur gases within the CO₂ mixture to be stored (Knauss et al., 2005; Schaef et al., 2014). This is especially significant because of the extra costs imposed by the process of removing sulfur from flue gas produced by fossil fuel combustion in order to create a pure CO₂ stream for carbon storage (Kaszuba et al., 2011). Sulfur-CO₂ mixtures can alter reservoir composition and security in several ways. For example, dissolved CO₂ forms a weak acid with water, whereas dissolved sulfur can form a strong acid, which might act to corrode reservoir and caprock minerals (Ellis et al., 2010; Kummerow and Spangenberg, 2010). Gypsum or anhydrite formation may occur in calcium- and sulfate-rich fluids at pH<5 in brine-

70 filled fractures, and this mineralization may impact permeability and fluid migration in CO₂ reservoirs (Xu et al., 2007). At higher pH, the addition of sulfur to CO₂-charged waters may drive both an increase in rates of mineral dissolution and an eventual increase in trapping of CO₂ through secondary carbonate precipitation (Ellis et al., 2010). Furthermore, sulfur can occupy multiple valence states, thus releasing or consuming electrons and influencing fluid-rock reactions by
75 impacting the redox state and pH of reservoir fluids (Xu et al., 2007; Kaszuba et al., 2011). Microbial activity, including microbial sulfate reduction, may also play an important role in buffering the redox chemistry of the subsurface, and this could affect toxic trace metal mobilization and transport in CO₂-rich fluids (Kirk, 2011; Frerichs et al., 2014). These important processes remain poorly understood.

80 We report a study of sulfur mineralization in a stacked series of shallow naturally charged CO₂ reservoirs and caprock systems from Green River, Utah that extend to 285m below the surface. Such natural CO₂ reservoirs are laboratories that provide a unique opportunity to study the behavior of CO₂ in the subsurface. In such reservoirs, the chemical reactions and flow length of CO₂-charged fluids are integrated over sufficiently long time-scales to enable prediction of the changes in
85 mineralogical composition that these fluids may produce over time periods relevant to geologic CO₂ storage. In the reservoirs at Green River, sulfur exists as aqueous sulfate and sulfide in the reservoir brines, with concentrations of 16-21 mmol/L and ~0.5-1 mmol/L, respectively (Kampman et al., 2009, 2014), as sedimentary gypsum beds in the Carmel Formation, as remobilized secondary gypsum veins within the Carmel Formation and the Entrada Sandstone, and as disseminated pyrite and
90 pyrite-mineralized open fractures throughout the reservoir. Analyses of gypsum obtained from deep basin evaporite deposits, from which the CO₂-charged brines originate (Wilkinson et al., 2009;

Kampman et al., 2014), are also presented. Sulfur and oxygen isotopes of gypsum, pyrite and aqueous sulfate ($\delta^{34}\text{S}_{\text{SO}_4}$, $\delta^{34}\text{S}_{\text{pyr}}$, $\delta^{18}\text{O}_{\text{SO}_4}$) are used to trace the sources of sulfur in the CO₂-charged groundwater systems. These isotope analyses are coupled with measurement of the isotopes of
95 gypsum hydration water ($\delta^{18}\text{O}$ and δD) to determine the isotopic composition of the water from which these gypsum deposits mostly recently precipitated and to distinguish primary gypsum precipitation from other processes that could form gypsum, such as dehydration and anhydrite rehydration. Our objective is to constrain the relative timing of gypsum vein formation and establish a genetic relationship between fluxes of CO₂-charged brine, sulfur mobilization, and mineralization
100 of gypsum. This may yield insight into how sulfur injected into a carbon storage site reacts in the presence of CO₂ and impacts the overall mineralogy and geochemistry of the reservoir.

1.1 Geological Setting

The natural CO₂ reservoirs examined in this study consist of a stacked series of Jurassic
105 sandstone aquifers. These aquifers are located near the town of Green River, Utah in the northern part of the Paradox Basin, an area in the Colorado Plateau that extends across southeastern Utah and southwestern Colorado. At Green River, the Little Grand Wash and Salt Wash Graben fault systems extend east to west (**Figure 1**) and cut across the Green River Anticline, which comprises Paleozoic and Mesozoic strata (Doelling, 2002). The strata include Jurassic-aged formations: the
110 Entrada Sandstone overlies the Carmel Formation, which in turn overlies the Navajo Sandstone. The Entrada Sandstone comprises aeolian sandstones interspersed with intercalated marginal marine and sabkha deposits (Crabaugh and Kocurek, 1993). An exhumed section of the Entrada Sandstone that preserves reservoir-scale mineralogical alterations due to the past migration of reducing CO₂-

charged brines is located along the Salt Wash Graben to the south of the Little Grand Wash Fault
115 (Wigley et al., 2012). The Carmel Formation was deposited in a shallow restricted sea and comprises
sandstone, siltstone, shale, mudstone, and bedded gypsum (Peterson and Turner-Peterson, 1989; De
Gibert and Ekdale, 1999). The lowest unit is the Navajo Sandstone, which consists of cross-bedded
aeolian sandstones (see Verlander, 1995 and references therein). Below the Jurassic strata, groups
of Triassic, Permian, and Pennsylvanian-aged strata are located, including the Pennsylvanian Paradox
120 Formation. The Paradox is an evaporite deposit with cyclic deposits of halite, anhydrite, and organic-
rich shale (Petrychenko et al., 2012). During the Quaternary, extensive dissolution of salt from the
Paradox Formation led to localized collapse of a series of salt-cored anticlines in the Paradox fold
and thrust belt, on which the Salt Wash and Little Grand Faults lie on the periphery (see Baars and
Stevenson, 1981; Gutiérrez, 2004 and references therein). This collapse was associated with
125 alteration and mineralization of Jurassic sediments through which these saline brines flowed (Chan
et al., 2000).

Fluids charged with CO₂ leak to the surface through the Little Grand Wash and Salt Wash
Faults and through abandoned petroleum exploration and water wells, to form a series of springs
and geysers (Burnside et al. 2013; Kampman et al., 2009, 2014). These normal faults are thought to
130 have formed during the Laramide orogeny, based on K-Ar dating of the fault gouge (circa. 40 Mya;
Dockrill et al., 2006). U-Th dating of surface carbonates demonstrates that CO₂ has been leaking
through these faults for at least 400,000 years (Burnside et al., 2013), with periodic pulses of CO₂
degassing occurring after periods of local climate warming during the last 135,000 years (Kampman
et al., 2012). The CO₂ exists in a subcritical state throughout the Entrada Sandstone, Carmel

135 Formation, and Navajo Sandstone and has been suggested to be crustal in origin (Heath et al., 2004),
originating in much deeper strata and migrating up the fault zones in the Green River anticline.
Migration of CO₂-charged brines through these faults is accompanied by localized hydraulic
fracturing, but there is little geological evidence to suggest that this was associated with significant
slip along the fault plane (Kampman et al., 2012). The fluids sampled from CO₂-degassing springs
140 contain brine from the deep evaporite-bearing Paradox Formation mixed with this CO₂-charged
groundwater (Williams-Stroud, 1994; Wilkinson et al., 2009; Kampman et al., 2009, 2013, 2014).
These CO₂-charged fluids are mildly reducing and have trace quantities of hydrogen sulfide and
methane (Kampman et al., 2009; Kampman et al., 2014).

At Green River, Utah, a drilling campaign was completed in 2012 to sample the CO₂-charged
145 fluids and reservoir rocks at a site adjacent to the Little Grand Wash Fault (Kampman et al., 2013). A
CS4002 Truck Mounted Core Drill recovered 322 m of core through the Entrada Sandstone, Carmel
Formation, and Navajo Sandstone. The bottom of the Entrada Sandstone was located at 149 m
below the surface and the bottom of the Carmel Formation at 199 m below the surface (Kampman
et al., 2014). A stratigraphic log of the recovered core is presented in **Figure 1**.

Figure 1: Stratigraphic log and location map redrafted from Kampman et al., 2014.

1a. Detailed stratigraphic log of the Entrada Sandstone, Carmel Formation and Navajo Sandstone recovered through the drilling campaign. Approximate sample locations in the Entrada Sandstone and Carmel Formation and data on fracture sets in the core are displayed. The blue line indicates the fault damage zone in the Carmel Formation (described below).

1b. Location map showing the extent of Paradox Basin and the town of Green River

160 1c. Map of geologic features near the drill site and the drillhole labeled as
CO2W55.

The Entrada Sandstone contains intervals of cross-bedded sandstone bleached by saline, reducing, CO₂-charged fluid. These intervals are extensively cross cut by fractures mineralized with gypsum and pyrite and bound by localized areas of carbonate mineralization (calcite, dolomite, and
165 ferroan dolomite) in the host-rock (**Figure 2**; Kampman et al., 2014). Similar paragenetic sequences are observed in outcrops of the Entrada Sandstone, exhumed along the nearby Salt Wash Graben Fault (Wigley et al., 2012). Fracture orientations are either sub-vertical or near-horizontal; these are thought to relate to regional fault movement and to hydraulic fracturing of the formation within the vicinity of the Little Grand Wash Fault, as has been observed for exhumed portions of the Salt Wash
170 Graben Fault (Kampman et al., 2012). The Carmel Formation contains local sedimentary gypsum beds and is transected by an intense zone of fracturing referred to here as ‘the fault damage zone’ that contains brecciated rock intensely veined with and suspended within a matrix of gypsum (Kampman et al., 2014). The gypsum-cemented breccia may be a product of localized remobilization and ductile flow of the gypsum in the gypsum beds during faulting. No gypsum veins or beds were
175 observed in sections of the core from the Navajo Sandstone.

Figure 2: Images of gypsum beds and veins

2a. Core photo that depicts gypsum beds and veins in the fault damage zone (blue bracketed section in Figure 1). Each core section is 2 ft long. The gypsum beds host blocks of brecciated rock. The gypsum veins comprise fractures filled with gypsum.

2b. Horizontal and sub-vertical gypsum-filled fractures in the Carmel Formation.

2c. High-angle calcite fracture in the Entrada Sandstone

2d. High-angle gypsum-filled fracture in the Entrada Sandstone

2e. Scanned thin section of contact between gypsum vein and siltstone in the Carmel Formation

1.2 The use of isotopes within gypsum and gypsum hydration water

Gypsum has the chemical formula $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ – therefore comprising calcium, sulfate, and two molecules of bound water, known as gypsum hydration water. The sulfur and oxygen isotopic composition of the sulfate within the gypsum crystal is similar to the sulfate in the fluid from which the gypsum precipitates, with a possible isotope fractionation during precipitation that is less than

195 2‰ for either isotope (Lloyd, 1968; Van Stempvoort et al., 1990; Samborska et al., 2013). The exchange rate between oxygen isotopes in sulfate and surrounding water is very slow under typical conditions of low temperature and neutral pH, so the $\delta^{18}\text{O}_{\text{SO}_4}$ usually reflects the last time that the sulfur atom acquired oxygen atoms and the pathway by which this occurred (Lloyd, 1967; Kusakabe and Robinson, 1977; Böttcher et al., 2001). Measurements of the $\delta^{34}\text{S}_{\text{SO}_4}$ and $\delta^{18}\text{O}_{\text{SO}_4}$ of gypsum
200 have been used previously to explore the dynamics of evaporite basins (e.g. Alonso-Azcarate et al., 2006) and the mixing of various sulfate reservoirs (e.g. Metzger et al., 2015). The $\delta^{34}\text{S}_{\text{SO}_4}$ and $\delta^{18}\text{O}_{\text{SO}_4}$ of the aqueous sulfate within the CO₂-charged fluids at Green River has been previously published and ranges from 9.5-10.4‰ and 9.0-10.6‰, respectively; spatial trends in these measurements are coupled to changes in the major elemental (e.g. chloride, bromine) and isotopic
205 composition ($^{87}\text{Sr}/^{86}\text{Sr}$, $\delta^{18}\text{O}_{\text{H}_2\text{O}}$) of the CO₂-charged brines (Kampman et al., 2014). These spatio-compositional trends reflect mixing between sulfate-rich CO₂-charged brines derived from the underlying Carboniferous Paradox Formation, with sulfate in meteoric groundwater-brine mixtures from the Carmel Formation (Kampman et al., 2014).

The $\delta^{18}\text{O}$ and δD isotopic composition of the gypsum hydration water has been used to
210 calculate the isotopic composition of the mother water from which the gypsum mostly recently precipitated (Sofer, 1978, Hodell et al., 2012; Evans et al., 2015). Analysis of the gypsum hydration water can provide important constraints on the fluid sources that formed the veins and subsequent mechanisms of gypsum dehydration and rehydration, thus revealing information about the history and relative timing of vein formation.

2. Experimental Methods

2.1 Sampling of Gypsum

Gypsum was obtained by drilling plugs with 1.5 cm diameters on core sections from well CO2W55 (Kampman et al., 2013). Veins from a range of depths in the Entrada Sandstone and Carmel Formation (hereafter called secondary gypsum veins) and sedimentary beds in the Carmel Formation (hereafter called gypsum beds) were sampled. Secondary gypsum veins were identified relative to gypsum beds based on their morphology and cross-cutting relationships. The secondary gypsum veins in the Carmel Formation are found in two separate locations: near the stratigraphic height of the gypsum beds (depths between 158-175 m) and deeper than the gypsum beds (depths greater than 190 m). The former are the veins within the heavily brecciated fault-damage zone. Gravimetric analysis of sample water loss after dehydration was used to identify the weight percent of water present in calcium-sulfate minerals (Gaquez, et al., 2015). When samples contained a significantly smaller weight percent of water that is expected for gypsum (20.9%), X-ray diffraction (XRD) analysis was used to distinguish gypsum from anhydrite.

2.2 Sulfur and Oxygen Isotopes in Gypsum and Pyrite

Gypsum powder was obtained by drilling directly into the gypsum vein or bed. To extract the sulfate for sulfur and oxygen isotope analysis, the powder was left in deionized water overnight. The effluent containing the aqueous sulfate from the dissolution was then separated, and a supersaturated barium chloride solution (50 g/l) was added to precipitate barium sulfate. The barium sulfate precipitate was rinsed with 6M HCl and several times in deionized water and dried in a 35°C oven overnight prior to analysis.

Pyrite (FeS₂) was extracted from hand samples through digestion of 5-10 grams of whole rock powder in a chromium chloride solution (Canfield et al., 1986). 60 mL of 1M CrCl₂ and 0.5 M HCl solution was added to the whole rock powder and nitrogen gas was bubbled for 2-3 hours, releasing hydrogen sulfide gas from the sulfide minerals. The hydrogen sulfide gas was passed through a vessel containing 0.1 M HNO₃ to remove chlorine gas and then into a trap filled with AgNO₃ and 10% NaOH solution. The silver sulfide precipitated was analyzed for its sulfur isotope composition.

The sulfur and oxygen isotopic composition of the sulfate from the gypsum veins and beds and the sulfur isotope composition of the sulfide from the pyrite were measured in the Godwin Laboratory at the University of Cambridge. For $\delta^{18}\text{O}_{\text{SO}_4}$, a Temperature Conversion Element Analyzer (TC/EA) was used to pyrolyze the barite at 1450°C and produce CO, which was measured by continuous flow Gas Source Isotope Ratio Mass Spectrometry (ThermoScientific Delta V Plus). Samples were run in duplicate or triplicate with the NBS-127 Standard (8.6‰), and the average and standard deviation of the replicate analyses is reported. All $\delta^{18}\text{O}_{\text{SO}_4}$ reported are relative to V-SMOW (Vienna-Standard Mean Ocean Water). For $\delta^{34}\text{S}_{\text{SO}_4}$, the barite was combusted at 1030°C in a Flash Elemental Analyzer (Flash-EA), and the sulfur dioxide produced was measured by continuous flow Gas Source Isotope Ratio Mass Spectrometry (ThermoScientific, Delta V Plus). Samples for sulfur isotope analysis were run alongside the NBS-127 standard (20.3‰). Multiple measurements of the standard were made in each run, and the standard deviation of the standards is reported as $\delta^{34}\text{S}$ standard deviation in Tables 1-3. Blind replicates were run for 10% of the samples. For most runs, the 2 σ standard deviation was less than 0.4‰ for $\delta^{34}\text{S}$ (based on the replicate analyses of the standards) and 0.8‰ for $\delta^{18}\text{O}$ (based on the duplicate or triplicate analyses of a single sample),

though a small number of samples had slightly larger standard deviations of 0.6‰ and 1.5‰,
260 respectively. All $\delta^{34}\text{S}_{\text{SO}_4}$ reported are relative to VCDT (Vienna- Canyon Diablo Troilite).

2.3 Oxygen and Hydrogen Isotopes in Gypsum Hydration Water

The $\delta^{18}\text{O}$ and δD of gypsum hydration were analyzed by heating the gypsum *in vacuo* using a
bespoke offline extraction system consisting of six vacuum lines contained within a modified gas
265 chromatography (GC) oven (Gázquez et al., 2015). Prior to the extraction, powdered gypsum
samples were dried in an oven at 35°C overnight. Each extraction consisted of five samples and one
gypsum standard. Gypsum samples (~200 mg) were loaded into disposable 12-mm Pyrex tubes,
placed in the GC oven, and connected to individual stainless vacuum lines. The hydration water was
recovered after drying in a 6-mm break-seal tube by cryogenic trapping in liquid nitrogen at -196 °C.
270 Samples were placed under vacuum ($\sim 5 \times 10^{-3}$ mbar) for at least 3 hours at room temperature to
remove adsorbed water from the gypsum. Subsequently, gypsum hydration water was released by
slowly heating the sample to 400°C. Once the oven reached 400°C, this temperature was maintained
for 40 minutes to ensure all water in the lines was recovered in the cryogenic traps.

Oxygen and hydrogen isotopes of the water were measured simultaneously by cavity ring
275 down spectroscopy using a L1102-*i* Picarro water isotope analyzer and A0211 high-precision
vaporizer at the Godwin Laboratory at the University of Cambridge (Hodell et al., 2012). Each
sample was injected nine times into the vaporizer. Memory effects from previous samples were
avoided by rejecting the first three analyses. Values for the final six injections were averaged with
typical in-run precision of $\pm 0.05\text{‰}$ for $\delta^{18}\text{O}$ and $\pm 0.4\text{‰}$ for δD (1σ). Calibration of results to V-
280 SMOW was achieved by analyzing internal standards before and after each set of 7 or 8 samples.

Internal standards were calibrated against V-SMOW, GISP, and SLAP. All results are reported in parts per thousand (‰) relative to V-SMOW. The external error of the method was $\pm 0.1\text{‰}$ for $\delta^{18}\text{O}$ and $\pm 0.6\text{‰}$ for δD (1σ), as estimated by repeated analysis ($n=9$) of an internal gypsum standard extracted together with the samples in each run.

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3. Results

The sulfur and oxygen isotopic composition of the secondary gypsum veins in the Entrada Sandstone (37 Samples - **Table 1**) and of the Carmel Formation's gypsum beds (19 samples) and secondary gypsum veins (35 Samples - **Table 2**) are presented in **Figure 3**, along with the sulfur and oxygen isotope data from samples of the Paradox Formation evaporites (8 Samples - **Table 3**).

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Figure 3: Results for $\delta^{34}\text{S}_{\text{SO}_4}$ and $\delta^{18}\text{O}_{\text{SO}_4}$ of gypsum beds in the Carmel Formation (black diamonds), secondary gypsum veins in the Carmel Formation (grey diamonds) and Entrada Sandstone (open circles), and evaporites from the Paradox Formation (black circles). $\delta^{34}\text{S}_{\text{SO}_4}$ and $\delta^{18}\text{O}_{\text{SO}_4}$ of dissolved sulfate in fluid samples, reported in Kampman et al., 2014, are also shown.

In **Figure 3**, the area in grey is the previously reported sulfur and oxygen isotopes from aqueous sulfate measured in both downhole fluid sampling and surface springs (Kampman et al., 2014). The gypsum beds in the Carmel Formation have a $\delta^{34}\text{S}_{\text{SO}_4}$ between 14.7‰ and 16.1‰ and a $\delta^{18}\text{O}_{\text{SO}_4}$ between 7.8‰ and 12.0‰. The secondary gypsum veins in the Carmel Formation have a $\delta^{34}\text{S}_{\text{SO}_4}$ between 10.1‰ and 16.1‰ and a similar range of $\delta^{18}\text{O}_{\text{SO}_4}$ between 7.6‰ and 12.8‰. In contrast, the secondary gypsum veins in the Entrada Sandstone have a narrow range of $\delta^{34}\text{S}_{\text{SO}_4}$ between 10.6‰ and 12.5‰, but a wide range of $\delta^{18}\text{O}_{\text{SO}_4}$ between 3.6‰ and 14.4‰, skewed by two analyses that are isotopically depleted in ¹⁸O compared to the rest of the analyses. These two analyses were part of twelve measurements taken across the same vein (**Table 1**). The sulfur and oxygen isotopic composition of the Paradox Formation evaporites ranges between 11.3‰ and 13.1‰ for $\delta^{34}\text{S}_{\text{SO}_4}$ and between 9.7‰ and 12.2‰ for $\delta^{18}\text{O}_{\text{SO}_4}$ (**Table 3**).

Twenty-five samples were analyzed for $\delta^{18}\text{O}$ and δD of gypsum hydration water (**Table 4**, **Figure 4**).

Figure 4: $\delta^{18}\text{O}$ and δD of gypsum mother water after correction for the isotopic fractionation for water isotopes during gypsum formation. The downhole fluid sample data from Kampman et al., 2014 is included for reference. The Local Meteoric Water Line is indicated by the solid line. The samples outside of the fault-damage zone all fall below the Local Meteoric Water Line in both oxygen and hydrogen isotope space, while the majority of the samples in the fault-damage zone fall above this line.

The $\delta^{18}\text{O}$ of gypsum hydration water ranged from -12.7‰ to -9.4‰, while δD was between -137.7‰ and -113.2‰. The isotope fractionation of oxygen isotopes between gypsum hydration water and

330 mother water ($\alpha^{18}\text{O}_{\text{gyp-H}_2\text{O}}=1.004$) is independent of temperature in the 12-37°C range (Gonfiantini and Fontes, 1963; Fontes and Gonfiantini, 1967; Hodell et al., 2012). The hydrogen isotope fractionation between gypsum hydration water and mother water ($\alpha_{\text{D}_{\text{gyp-H}_2\text{O}}}=0.981$) is largely temperature-independent in this range, though there may be a very slight temperature effect of .00012 per °C (Hodell et al., 2012). We use these isotope fractionation factors to calculate the

335 isotopic composition of the gypsum mother water from which the gypsum formed; for the secondary gypsum veins in the Entrada Sandstone, this mother water had a narrow isotopic composition ($\delta^{18}\text{O}$ between -15.2‰ and -14.4‰ and δD between -117.6‰ to -121.0‰), similar to previous measurements of the isotopic composition of the downhole and surface fluids (Figure 4 – previous data from Kampman et al., 2014). In contrast, gypsum beds in the Carmel Formation

340 were hydrated by water with more variable isotopic compositions (between -16.2‰ and -14.6‰ for $\delta^{18}\text{O}$ and from -110.7‰ to -99.8‰ for δD). There is a similarly wide range of oxygen and hydrogen isotopes in the hydration water from the secondary gypsum veins in the Carmel Formation ($\delta^{18}\text{O}$ between -16.6‰ and -13.4‰ and δD between -117.9‰ and -96.1‰) (**Figure 4**). Six additional samples (**Table 4**) from within the fault damage zone were identified as anhydrite

345 based on XRD and on the fact that they yielded less than 12% water calculated gravimetrically, which is considerably less than that expected for pure gypsum (20.9%). Five of these six samples yielded less than 5% water.

Isotopic variability with depth, including measurements of $\delta^{34}\text{S}_{\text{pyrite}}$, is shown in **Figure 5**. The $\delta^{34}\text{S}_{\text{pyrite}}$ in the Entrada Sandstone ranges between -47.4‰ and 18.8‰ (**Table 5** – 13 samples; **Figure 5a**); the $\delta^{34}\text{S}_{\text{pyrite}}$ appears to get isotopically heavier with depth in the Entrada Sandstone. The $\delta^{34}\text{S}_{\text{pyrite}}$ near the base of the Entrada Sandstone has a similar sulfur isotopic composition to

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the secondary gypsum veins. The $\delta^{34}\text{S}_{\text{SO}_4}$ of the gypsum (**Figure 5b**) throughout the Entrada Sandstone and in the base of the Carmel Formation is similar, while most of the samples in the fault damage zone yield $\delta^{34}\text{S}_{\text{SO}_4}$ that is ~3‰ higher. The deuterium-excess or d-excess (**Figure 5c**) is the deviation of the deuterium measurements from the Local Meteoric Water Line and is calculated as $\delta\text{D} - 8 \cdot \delta^{18}\text{O}$ (Dansgaard, 1964). In the Entrada Sandstone and the base of the Carmel Formation, the d-excess values are similar, which parallels the pattern observed in the $\delta^{34}\text{S}_{\text{SO}_4}$ of these secondary veins. However, the data in the fault-damage zone is more scattered and ranges from 1.9‰ to values as high as 33.7‰.

Figure 5: Depth Plots

5a. Depth plot of $\delta^{34}\text{S}_{\text{pyrite}}$ for Entrada Sandstone samples that contain disseminated pyrite.

5b. $\delta^{34}\text{S}_{\text{SO}_4}$ of the gypsum beds and secondary gypsum veins plotted against depth. Within the Carmel Formation, the secondary gypsum veins located in the fault-damage zone are isotopically similar to the gypsum beds, while those located further from the gypsum beds are isotopically similar to the secondary veins in the Entrada Sandstone.

5c. Depth plot of deuterium excess (also called d-excess) for gypsum hydration water in the gypsum beds and secondary gypsum veins. Some samples in the fault-damage zone have high d-excess, and samples at shallower or deeper locations have low d-excess.

4. Discussion

The primary goal of this study is to explore the formation of secondary gypsum veins in the natural CO₂-charged reservoirs at Green River. We propose that an understanding of secondary gypsum vein formation provides information on faulting and fracturing within the reservoir and on the behavior of co-existing sulfate- and CO₂-charged brines. The discussion of our data is split into two parts. First, we examine mixing between sources of sulfur and processes that could affect the isotopic composition of gypsum hydration water to understand the timing of gypsum bed and secondary gypsum vein formation in the Carmel Formation. We then use the isotopic composition of gypsum hydration water and oxygen isotopes in sulfate to understand the factors that influenced secondary gypsum vein formation in the Entrada Sandstone.

4.1 Formation of the Gypsum Beds and Secondary Gypsum Veins in the Carmel Formation

4.1.1. Mixing between sulfate derived from the Paradox Formation evaporites and

Carmel Formation gypsum beds

390 Aqueous sulfate was previously reported in the downhole and surface fluids from Green River; the interpretation of these analyses was that sulfate in the reservoir fluids originates largely from the anhydrite in the Paradox Formation, with some mixing of sulfate from gypsum in the fracture zone within the Carmel Formation (Kampman et al., 2014). In theory, if the source of the sulfate in the CO₂-charged brine was the dissolution of evaporites from the Paradox Formation
395 mixed with dissolved gypsum from the Carmel Formation, then the downhole fluid samples should plot between the isotopic composition of the Paradox Formation and that of the Carmel Formation in sulfur and oxygen isotope space (**Figure 3**). However, aqueous sulfate in the reservoir fluids has a lower sulfur isotopic composition than either proposed end member (**Figure 3**). There is no evidence for an additional source of sulfate that is lower in δ^{34} . Instead, we suggest that a small amount of
400 hydrogen sulfide existed in the downhole fluids reported in Kampman et al. (2014) and was homogenized with the sulfate from the dissolution of the Paradox Formation anhydrites prior to sulfur isotope analysis. Previous studies at Crystal Geyser and the Little Grand Wash Fault zone detected hydrogen sulfide through gas flux measurements or by the detectable odor of H₂S gas (Allis et al., 2005; Haszeldine et al., 2005). The aqueous hydrogen sulfide could derive either from
405 microbial sulfate reduction in the reservoir fluids or subsurface pyrite dissolution in the Carmel Formation or Entrada Sandstone.

A simple isotope mass balance illustrates this scenario. If the sampled fluid contained 19-20 mmol/L of sulfate and ~ 0.5-1 mmol/L of H₂S, which is consistent with the measured oxidation state

of the fluids (Kampman et al., 2014), to shift the $\delta^{34}\text{S}$ of the aqueous sulfate down from 12.5‰
410 (Paradox Formation) to 10.2‰ (measured aqueous sulfate) would require hydrogen sulfide with a of
 $\delta^{34}\text{S}$ of approximately -35‰. This low $\delta^{34}\text{S}$ is typical for hydrogen sulfide produced during microbial
sulfate reduction or otherwise found in pyrite (e.g. Böttcher et al., 2004).

The relatively wide range of $\delta^{34}\text{S}_{\text{SO}_4}$ measured in gypsum veins from the Carmel Formation
indicates that these veins may have formed from multiple sulfur sources. The secondary gypsum
415 veins in the Carmel Formation lie on an isotope mixing line between the sulfur isotopic composition
of the gypsum beds in the Carmel Formation and the isotopic composition of the evaporites in the
Paradox Formation (**Figure 6**). A mixing model is proposed to explain the sulfur and oxygen isotopic
composition of the secondary gypsum veins in the Carmel Formation (**Figure 6**). In this calculation,
two end members are considered, the first being the Carmel gypsum beds, and the second being the
420 evaporites in the Paradox Formation. The measured $\delta^{34}\text{S}_{\text{SO}_4}$ of the downhole fluids is not used as the
second end-member because, as outlined above, these measurements may have been compromised
during sampling by oxidation of sulfide in the fluid.

Figure 6 - $\delta^{34}\text{S}_{\text{SO}_4}$ and $\delta^{18}\text{O}_{\text{SO}_4}$ of the gypsum beds and secondary gypsum veins in the Carmel Formation. A mixing line is shown with two end members: the gypsum from the beds and the sulfate from the Paradox Formation.

As shown in **Figure 6**, the secondary gypsum veins in the Carmel Formation are either similar to the gypsum beds in the Carmel Formation or exist close to, or slightly above (higher $\delta^{18}\text{O}_{\text{SO}_4}$), the mixing line between the beds in the Carmel Formation and the sulfate in the Paradox Formation. These results suggest that the secondary gypsum veins in the Carmel Formation are produced when gypsum beds within the Carmel Formation dissolve, reprecipitate, and are mixed with varying amounts of sulfate from the Paradox evaporites. This conclusion is supported by data shown in **Figure 5b**, where the sulfur isotope composition of the veins in the fault damage zone are of a similar isotopic composition to the gypsum beds, while those that are deeper in the formation and

further away from the gypsum beds in the fault damage zone are closer to the $\delta^{34}\text{S}_{\text{SO}_4}$ of the underlying Paradox Formation.

This conclusion is also supported by the oxygen and hydrogen isotopic composition of the gypsum hydration water from the samples that are located in the Carmel Formation but outside the fault-damage zone. The secondary gypsum veins within the Carmel Formation (and Entrada Sandstone) that are not in the fault-damage zone have low d-excess, which are comparable to those of the modern fluids (**Figure 5c**). On the other hand, the $\delta^{18}\text{O}$, δD , and d-excess of the mother water for the secondary gypsum veins and gypsum beds in the fault-damage zone span a wide range, and some of these samples plot far from the downhole fluids in $\delta^{18}\text{O}$ and δD isotope space. The difference in gypsum hydration water data between the secondary veins in the fault-damage zone and in the deeper parts of the Carmel indicate that two fluid sources – one that flows within the fault-damage zone and one that originates from a deeper formation – must have formed these veins.

4.1.2 Processes that may have affected the formation of gypsum in the fault damage zone

The $\delta^{18}\text{O}$ and δD of some gypsum beds and secondary gypsum veins in the fault damage zone deviate from the modern Local Meteoric Water line, since they show higher d-excess (**Figure 5c**). The typical d-excess in natural waters usually does not exceed 20‰ (Dansgaard, 1964), while values of up to 33‰ are calculated for some samples in the fault-damage zone (**Table 4**). Previous studies have shown that negative d-excess can be attributed to meteoric or seawater evaporation (Gat and Gonfiantini, 1981; Evans et al., 2015), yet such large and positive d-excess is rarely observed.

One possibility is that the gypsum in the fault damage zone formed through the hydration of anhydrite to gypsum with a low water-to-mineral ratio, such that the supply and exchange of water is limited relative to the amount of anhydrite (Bath et al., 1987). Anhydrite hydration to gypsum under equilibrium conditions in which the newly-hydrated gypsum no longer exchanges with the surrounding water can be modeled by the isotope distillation equation – also known as Rayleigh fractionation – for equilibrium closed systems (Matsubaya and Sakai, 1973; Gat and Gonfiantini, 1981):

$$R/R_0 = f^{(\alpha-1)} \quad \text{Eq 1.}$$

Where R denotes the ¹⁸O to ¹⁶O or ²H to ¹H ratio, α is the isotope fractionation factor between hydration water and mother water, and f is the fraction of original water remaining in solution. In principle, as groundwater hydrates anhydrite to gypsum, the isotopes in this water distill into the gypsum, leaving the residual water isotopically evolved. As a result, the oxygen or hydrogen isotope composition of the newly-hydrated gypsum exhibits non-equilibrium isotope composition. Note that a limited supply of water is essential for this hypothesis; otherwise, it would not be possible for the isotopes of this water to evolve to such a large degree. Using Equation 1 to calculate the evolution of the water isotopes during this process (with the isotope fractionation factors given by Sofer (1978)) yields a line for isotopic composition of the mother water with a slope of ~ -5 in a cross plot of δD versus δ¹⁸O (Matsubaya and Sakai, 1973). The slope is negative because the hydration of anhydrite with limited amounts of water favors the heavy oxygen atom (¹⁸O) but the light hydrogen isotope (¹H) (Sofer, 1978), and this process results in depletion in ¹⁸O and enrichment in ²H in the remaining water. Thus, the line cuts across the Local Meteoric Water Line, and the d-excess is high. The starting point of such a line occurs where f=1, since this represents the theoretical

original water; in this case, the original water is most likely to consist of local groundwater, which
 480 was collected as downhole fluid samples in Kampman, et al. (2014). Thus, the range of possible
 isotopic compositions for these original waters would be near the downhole fluids, and is indicated
 by the light gray shaded region slightly below the Local Meteoric Water Line in **Figure 7**. This region
 encompasses all the downhole fluids as well as the surface fluids and veins that plot near the
 downhole samples.

Figure 7: $\delta^{18}\text{O}$ and δD of gypsum mother water measured in this study and in previous studies on downhole and surface fluids. The light gray shaded region and dark gray shaded region represent, respectively, the range of isotopic compositions for local groundwater and the isotopic compositions that could result from the theoretical isotope fractionation trend that occurs when anhydrite is hydrated with limited amounts of water. This isotope fractionation is modeled through the isotope distillation equation, which produces lines with slopes of ~ -5 , as shown, for δD v. $\delta^{18}\text{O}$.

The fraction of original water remaining (f) is indicated by the triangle symbols on each line.

For example, if the original water is assumed to have the isotopic composition of the deepest gypsum vein at 173.6 m, the evolution of $\delta^{18}\text{O}$ and δD isotopes calculated with Equation 1 is shown by the dashed line that cuts across the center of the Local Meteoric Water Line, and five measurements from secondary gypsum veins fall close to this line. The lines that form the boundary of the dark gray shaded region are calculated by applying Equation 1 to the lightest and heaviest of the samples in the light gray shaded region. Thus, the dark gray region indicates the expected range of isotopic compositions for gypsum formed through anhydrite hydration with limited water, given the range of isotopic compositions for original water shown in **Figure 7**. All of the anomalous samples with large, positive d-excess are encompassed within the dark gray region. This demonstrates that the process modeled by Equation 1 may have formed the gypsum with high d-excess measured in the Carmel Formation.

The Carmel Formation is a low-permeability stratigraphic unit that serves as a seal for this CO₂ reservoir and a regional caprock for the fluids in the Navajo Sandstone (Dockrill and Shipton, 2010; Kampman et al., 2014). The fault damage zone within the Carmel Formation is composed mostly of siltstones and shales, with some regions of fine-grained sandstone (**Figure 1**). Thus, permeability and hydraulic conductivity within the fault damage zone are low, and flow of water is limited, so anhydrite hydration could have occurred under conditions of limited water availability in this geological setting.

This anhydrite hydration may have occurred within cycles of partial dehydration and rehydration after sedimentary deposition. Additional evidence for some dehydration of the gypsum

includes the fact that twenty-nine individual veins were measured, and the six that were identified as anhydrite were found within the fault-damage zone (Table 4). Primary anhydrite can form when concentrated brines flow into dry supratidal environments, while secondary anhydrite can form through heating and dehydration of gypsum (Shearman, 1985; Hardie, 1987). Since the Carmel Formation represents a marine highstand tract system (Blakey et al., 1996), it is likely that the calcium-sulfate minerals originally deposited were gypsum and that primary anhydrite was formed through subsequent dehydration during burial, and then subsequent rehydration produced the gypsum that is currently found in the fault damage zone of the Carmel Formation. If the dehydration of gypsum was partial, then lighter isotopes would be released first, while heavier ¹⁸O and deuterium would remain within the hydration water. Rehydration of this partially dehydrated gypsum could further alter the isotopic composition. The δ D of the gypsum that was newly rehydrated through this process would be higher than that of the original gypsum, while the δ^{18} O could be either higher or lower, depending on the fraction of original water remaining (f). Thus, this process of partial dehydration and rehydration may have affected some of the samples in the Carmel.

The timing of these dehydration and rehydration events may be related to the age of the faults, since the samples that plot above the Local Meteoric Water Line in δ^{18} O and δ D isotope space are all located within the fault damage zone. The inferred Laramide age (around 40 Mya) of these faults (Dockrill, 2006) also coincides with the estimated timing of deepest burial for the Jurassic strata in this portion of the Paradox Basin, since the Carmel Formation was buried to a depth of approximately 2.4km, and heated to circa 105°C, temperatures sufficient to stabilize the formation of anhydrite or hemihydrated calcium sulfate (basanite) (Nuccio and Condon, 1996). The cataclasite and anhydrite cemented fault breccia may therefore have formed during a late Laramide faulting,

with subsequent hydration to gypsum occurring during exhumation. Thus, gypsum hydration water
540 measurements may not always record the composition of local meteoric water or groundwater, but
may instead constitute evidence for the specific events and processes that enabled gypsum
formation.

4.2 The generation of the secondary gypsum veins in the Entrada Sandstone

545 The $\delta^{34}\text{S}$ and $\delta^{18}\text{O}$ measured in the secondary gypsum veins in the Entrada Sandstone differ
from those measured in the Carmel Formation, since these veins do not fall near the same binary
mixing line as the veins in the Carmel Formation (**Figure 3**), suggesting that the isotopic composition
of these samples cannot be explained by simple mixing between sulfate derived from gypsum beds
and Paradox evaporite minerals. In contrast to the secondary gypsum veins in the Carmel Formation,
550 which have a narrow range of $\delta^{18}\text{O}_{\text{SO}_4}$ and a wide range of $\delta^{34}\text{S}_{\text{SO}_4}$, the secondary gypsum veins in the
Entrada Sandstone have a small range of $\delta^{34}\text{S}_{\text{SO}_4}$, which is similar to the $\delta^{34}\text{S}_{\text{SO}_4}$ from the underlying
Paradox Formation, but a much wider range of $\delta^{18}\text{O}_{\text{SO}_4}$. The $\delta^{18}\text{O}_{\text{SO}_4}$ of the secondary gypsum veins in
the Entrada Sandstone lies mostly higher than the $\delta^{18}\text{O}_{\text{SO}_4}$ measured from their source (the Paradox
evaporites), although there are two measurements that lie far below (**Figure 3**). We note that these
555 low $\delta^{18}\text{O}_{\text{SO}_4}$ measurements were made in a vein for which multiple measurements were conducted;
it is difficult to understand how much significance to assign to these two values. There was no aspect
of their appearance to indicate that the low $\delta^{18}\text{O}_{\text{SO}_4}$ values are due to an anomaly that would justify
excluding the samples from consideration.

The overall wider range of $\delta^{18}\text{O}_{\text{SO}_4}$ (including the two 'low samples') may provide information
560 on the behavior of sulfate during fluid-rock reactions of CO₂-charged brines in the Entrada Sandstone. The oxygen isotope composition of sulfate is set during its formation, since the sulfur-oxygen bond in sulfate is exceptionally strong and does not break to exchange oxygen atoms with surrounding water, except at exceptionally low pH (<1) or exceptionally high temperatures (> 300°C, see Hoering and Kennedy, 1957; Zeebe, 2010; Rennie and Turchyn, 2014). Therefore, the $\delta^{18}\text{O}_{\text{SO}_4}$ should reflect the
565 incorporation of oxygen atoms into the sulfate molecule from the last time the sulfur atom underwent oxidation from molecular oxygen (e.g. O₂), from water, or from both. When sulfide oxidation proceeds in the absence of atmospheric oxygen (e.g. via iron), then all the oxygen atoms in the resultant sulfate derive from surrounding water (Calmels et al., 2007). During sulfide oxidation, intermediate valence state sulfur species, such as sulfite (SO₃²⁻) can also be produced; both these
570 species and the original sulfate may exchange oxygen atoms with ambient water at low temperatures, and the resulting sulfate would reflect this isotope equilibration (Brunner and Bernasconi, 2005; Surkov et al., 2012; Boschetti, et al., 2013). Therefore, the $\delta^{18}\text{O}_{\text{SO}_4}$ of sulfate produced from sulfide or sulfur oxidation tends to range between 0 and ~25‰ above the water in which the oxidation took place.

575 A simple explanation for the narrow range of $\delta^{34}\text{S}_{\text{SO}_4}$ and larger range of $\delta^{18}\text{O}_{\text{SO}_4}$ measured in the secondary gypsum veins in the Entrada Sandstone would be that a local source of sulfur or sulfide with a near-homogenous $\delta^{34}\text{S}$ was oxidized through different oxidation pathways, producing sulfate with a range of $\delta^{18}\text{O}_{\text{SO}_4}$. The likeliest source of reduced sulfur that could be oxidized would be hydrogen sulfide or primary pyrite within the Entrada Sandstone and Carmel Formation; however
580 these both have very low $\delta^{34}\text{S}$, which is inconsistent with the measured $\delta^{34}\text{S}$ of the gypsum (**Figure**

5a). Alternately, gypsum dissolution would contribute sulfate with a uniform $\delta^{34}\text{S}$, but it would be unexpected for this process alone to produce a range of $\delta^{18}\text{O}_{\text{SO}_4}$.

A more intriguing explanation for the range of isotope data in the secondary gypsum veins in the Entrada Sandstone is the possibility of a quantitative sulfur cycle within the fluids in the reservoir, close to some of the smaller gypsum veins. This redox cycling of sulfur would include microbial sulfate reduction to form hydrogen sulfide or another intermediate valence state sulfur species followed by near quantitative reoxidation of this species to form new sulfate. During this reoxidation, the resulting aqueous sulfate would gain new oxygen atoms from reactions with the surrounding water (Böttcher et al., 1998). Partial equilibration with water during this oxidation would result in exceptionally enriched values up to 25‰ higher than the $\delta^{18}\text{O}$ of the water. The majority of our analyses lie at 9‰ to 15‰, which is ~25‰ higher than the fluid $\delta^{18}\text{O}$ of -15‰ to -13‰ measured in Kampman, et al. (2014). However, because the reduction and oxidation of sulfur species would be quantitative, no sulfur atoms would be added or removed, so the sulfur isotopic composition of the sulfate formed by this quantitative cycling would be equal to the $\delta^{34}\text{S}$ of the original sulfate. For microbial sulfate reduction, a source of sulfate and organic matter is required (e.g. Böttcher et al., 2004). In the case of Green River, the organic matter is likely carried in the anoxic brine itself (Kampman et al., 2014). Sulfide produced during this sulfate reduction would have a variety of possible fates. Some sulfide could undergo precipitation to pyrite, as shown by the presence of disseminated pyrite within the reservoirs, while other amounts could remain in the reservoir fluids or could be reoxidized back to sulfate. The fluids sampled from the Entrada Sandstone may provide evidence for sulfide reoxidation, since they are ferrous iron-rich from

reductive hematite dissolution (Kampman et al., 2014). The reductive dissolution of hematite by sulfide proceeds via the following reaction (Dos Santos Afonso and Stumm, 1992):

605 During this reaction, the ferric iron in hematite reoxidizes sulfide back to sulfate, with some of the liberated ferrous iron eventually being incorporated into pyrite (Kampman et al., 2014). Thus, it is possible that a near-quantitative microbial sulfur cycle, comprising microbial sulfate reduction and sulfide oxidation via ferric iron reduction in the presence of the acidic CO₂-rich fluids, may provide a source of sulfide to drive the dissolution of hematite and sandstone bleaching. This redox cycling of
610 sulfur would involve only a very small amount of sulfate in the reservoir fluids because the $\delta^{34}\text{S}$ in the newly formed sulfate is nearly unchanged, but the $\delta^{18}\text{O}$ is variable. The small amounts of sulfate formed through redox cycling could be trapped in gypsum, if gypsum precipitation was fast relative to the residence time of sulfate in the reservoir.

This process would require gypsum precipitation in the Entrada Sandstone that occurs much
615 more rapidly than the vein formation over millions of years that may have taken place in the Carmel Formation. The gypsum hydration water data from the secondary gypsum veins that formed outside of the fault damage zone suggests recent precipitation. These secondary gypsum veins, which are located in the Entrada Sandstone and lower part of the Carmel Formation, have gypsum hydration water with the same isotope composition as the CO₂-charged brines measured in these formations
620 and the underlying Navajo Sandstone (Kampman et al., 2014; **Figure 4**). Thus, the fluids that hydrated the gypsum in the Entrada Sandstone likely have the same genesis as the CO₂-charged brines, which have been leaking through these faults for at least the past 135,000 years (Kampman et al., 2012). Consequently, the gypsum hydration water data suggests that the veins in the Entrada

Sandstone formed during these Quaternary discharge events on thousand-year timescales. This
625 timescale of precipitation is fast when compared to the secondary gypsum veins in the fault-damage
zone that transect gypsum beds in the Carmel Formation and may have formed through dissolution,
dehydration, and reprecipitation events concurrent with faulting during exhumation over millions of
years.

The evidence from multiple isotope analysis for different time periods of gypsum vein
630 formation at Green River is helpful for understanding the behavior of sulfur in carbon storage sites.
First, it is useful to compare the formation of secondary gypsum veins and carbonate minerals at
Green River to other studies of reservoirs in which both CO₂ and sulfur species are present.
Numerical modeling predicts that secondary anhydrite and pyrite will precipitate to fill fractures in
reservoirs that contain CO₂ mixed with sulfate or aqueous sulfide (Kaszuba et al, 2011; Xu et al.,
635 2007). The addition of sulfur to reservoir fluids may lead to dissolution of other minerals, which can
increase alkalinity and lead the formation of secondary carbonates (Ellis et al., 2010). Specifically,
sulfide oxidation by ferric iron (e.g. Equation 2) can increase pH and can help to promote carbonate
precipitation (Soetaert et al., 2007), and precipitation of secondary carbonate veins indeed occurs at
Green River near the reaction fronts where sandstone bleaching through iron dissolution is taking
640 place (Wigley et al., 2012). Our results confirm that adding sulfur into a CO₂ reservoir can result in
the deposition of secondary carbonate and secondary gypsum or anhydrite, with the presence of
small amounts of sulfur exerting an important control on mineral paragenesis.

In addition, the gypsum hydration water data indicates that vein formation may have
affected reservoir permeability. The most common calcium-sulfate mineral in the reservoirs at Green
645 River is gypsum because the current temperatures at this shallow natural analogue site are 15-18°C

(Kampman et al., 2014), which are not sufficiently high for stable anhydrite formation (Xu et al., 2007; Kaszuba et al., 2011). In the fault-damage zone, the evidence from the gypsum hydration water measurements for cycles of dehydration and rehydration may indicate that aquifer temperatures decreased from over ~57°C, at which anhydrite and gypsum solubility are equal, to the current water
650 temperature at which gypsum is the stable phase (García-Ruiz et al., 2007). This supports a Laramide age for the formation of these faults and suggests that fault movement and anhydrite cementation of the fault breccia occurred during peak burial in the Paleogene, or shortly after (Nuccio and Condon, 1996). Since the gypsum hydration water in the fault-damage zone shows little influence of the modern local water, this may suggest that gypsum and secondary anhydrite vein formation in
655 this region sealed off this zone from further fluid flow, thus substantially decreasing its permeability. Further reactive-transport modeling will help ascertain the effect of these mineralization reactions on retardation of CO₂ transport within the fault zone and CO₂ charged reservoirs.

Finally, the presence of pyrite and gypsum with a wide range of $\delta^{34}\text{S}$ and $\delta^{18}\text{O}_{\text{SO}_4}$, respectively in the Entrada Sandstone indicates that microbial sulfate reduction is currently occurring in the
660 reservoir. This production of hydrogen sulfide can cause dissolution of hematite grains, sandstone bleaching, and production of ferrous iron, thus affecting the mineralogical composition of the natural carbon reservoir. This can serve as a model for the behavior of SO₂ gas, which is the most common sulfur species emitted from fossil fuel combustion and can disproportionate to form hydrogen sulfide (Ellis et al., 2010). Our data can be combined with further studies of sulfide and
665 pyrite formation at Green River to demonstrate how microbial sulfate reduction may occur in natural carbon reservoirs and produce a variety of different sulfur species that alter these reservoirs through fluid-rock reactions.

5. Conclusions

670 This study presented $\delta^{34}\text{S}$, $\delta^{18}\text{O}$, and δD from aqueous sulfate, pyrite, gypsum, and gypsum hydration water within a natural CO₂ reservoir near Green River, Utah. The isotopic data for gypsum and gypsum hydration water from the Paradox evaporites, Carmel beds, Carmel veins, and Entrada veins displayed a wide range in $\delta^{34}\text{S}$, $\delta^{18}\text{O}$, and δD . Our data and a mixing model demonstrated that the Paradox evaporites and Carmel beds constituted the main sources of dissolved sulfate in the
675 CO₂-charged reservoir brines. Hydration water measurements indicated that secondary gypsum veins in the Entrada Sandstone formed during more recent periods of hydraulic fracturing and fluid flow during the Quaternary, while partial dehydration and rehydration associated with regional faulting may have formed the gypsum beds and veins in the Carmel Formation. The formation of secondary gypsum veins in conjunction with secondary carbonates suggested that secondary
680 mineralization can trap and inhibit leakage of both CO₂ and sulfur in geologic reservoirs. Additional research is necessary to confirm this finding in different environments and to determine its implications for the long-term viability of CO₂-SO₂ co-sequestration.

The aqueous sulfate and pyrite measurements as well as the $\delta^{18}\text{O}_{\text{SO}_4}$ data from the secondary veins in the Entrada Sandstone indicated that an active microbial sulfur cycle may be present.
685 Evidence for this included the presence of sulfate and sulfide with a large range of isotopic compositions and the differences in $\delta^{18}\text{O}$ and δD between the hydration waters from the secondary gypsum veins in the Entrada Sandstone and in the fault-damage zone of the Carmel Formation. The sulfide produced from microbial sulfate reduction may form pyrite, remain in the reservoir fluids, or be reoxidized. All three of these processes may be taking place in both the Entrada Sandstone and

690 the Carmel Formation. The effect of adding CO₂ into a system where microbial sulfate cycling is
present remains enigmatic (Morozova et al., 2010; Kirk, 2011). For the sulfur-bearing minerals at
Green River, more analyses of pyrite veins and additional sulfide samples are necessary to determine
whether microbial sulfate reduction has occurred. This demonstrates the importance of further work
to better understand whether microbes can alter the properties of geologic carbon storage sites by
695 causing different sulfur species to form and affect geochemical properties of reservoirs.

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Table 1 – Isotopic composition of the secondary gypsum veins in the Jurassic Entrada Sandstone. Samples with the same name and multiple numbers (e.g. E1, E2, E3...) were single veins that were microdrilled to look for intravein heterogeneity. All oxygen measurements were duplicated, with the exception of those sample names with a 3 or 6 as a subscript. These were measured three or six times. All measurements were conducted in July 2013 with the exception of those with a letter O in the subscript, which were conducted in October 2014.

Sample Name	Depth (m)	δ ³⁴ S	stdev	δ ¹⁸ O	stdev
V22 U1	19.12	11.9	0.16	12.0	0.17
V22 L1	19.12	11.8	0.41	12.8	0.56
V22 L2	19.12	11.6	0.41	12.5	0.13
V22 L3	19.12	11.7	0.41	12.7	0.25
GV049 ₃	47.06	11.8	0.21	12.0	0.06
222.24 _{O,3}	67.74	11.6	0.24	11.9	1.24
222.84 _{O,3}	67.92	10.6	0.24	10.8	0.86
GV001 223 E1	67.97	11.8	0.06	12.3	0.01
GV001 223 E2	67.97	11.6	0.28	9.7	0.45
GV001 223 E3	67.97	11.7	0.28	12.4	0.15
GV001 223 E4	67.97	11.6	0.28	12.6	0.25
GV001 223 E5	67.97	11.4	0.28	12.1	0.08
GV001 223 E M1	67.97	11.8	0.06	14.0	0.25
GV001 223 E M2	67.97	11.6	0.28	14.2	0.14
GV001 223 E M3	67.97	11.7	0.28	14.2	0.20
GV001 223 E M4	67.97	11.6	0.28	14.0	0.10
GV001 223 E M5	67.97	11.4	0.28	13.3	0.22
GV001 223 E M6	67.97	11.8	0.06	13.9	0.02
GV001 223 E M7	67.97	11.6	0.28	12.8	0.13
GV001 223 E M8	67.97	11.7	0.28	14.4	0.28
GV001 223 E M9	67.97	11.6	0.28	14.0	0.23
GV001 223 E M10	67.97	11.4	0.28	14.2	0.24
GV048 _{O,6}	69.31	11.5	0.22	11.2	0.37
250.2 E1	76.26	11.9	0.63	12.4	0.29
250.2 E2	76.26	11.9	0.39	12.4	0.49
250.2 E3	76.26	12.5	0.39	6.6	0.30
250.2 E4	76.26	12.5	0.22	3.6	0.77
250.2 E M1	76.26	11.9	0.63	12.9	0.13
250.2 E M2	76.26	11.9	0.39	13.0	0.27
250.2 E M3	76.26	12.5	0.39	13.0	0.02
250.2 E M4	76.26	12.5	0.22	12.5	0.00
250.2 E M5	76.26	11.9	0.63	13.2	0.02
250.2 E M6	76.26	11.9	0.39	11.5	0.05
250.2 E M7	76.26	12.5	0.39	11.5	0.33
250.2 E M8	76.26	12.5	0.22	12.2	0.15
ESS123 _{O,3}	76.26	10.8	0.24	10.0	0.19
303.5 2	92.51	11.5	0.41	10.2	0.32

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Table 2 – Isotopic composition of the gypsum beds and secondary gypsum veins in the Jurassic Carmel Formation. Samples with the same name and multiple numbers (e.g. C1, C2, C3...) were single veins that were microdrilled to look for intravein heterogeneity. All oxygen measurements were run in triplicate, with the exception of those sample names with a 2 or 6 as a subscript. These were measured two or six times. All measurements were conducted in July 2013 with the exception of those with an N or JA subscript, which were conducted in November 2014, or January 2015.

Sample Name	Depth (m)	Formation	δ ³⁴ S	stdev	δ ¹⁸ O	stdev
GV010	158.48	Carmel Bed	15.9	0.21	10.9	0.14
GV01B _{JA}	158.48	Carmel Bed	15.1	0.24	7.8	0.81
GV13B	158.79	Carmel Bed	15.3	0.21	10.5	0.11
522.0 C1 ₂	159.11	Carmel Bed	15.6	0.52	9.4	0.18
522.0 C2 ₂	159.11	Carmel Bed	15.2	0.28	11.5	0.57
522.0 C3 ₂	159.11	Carmel Bed	15.4	0.89	11.1	0.33
522.0 C4 ₂	159.11	Carmel Bed	15.3	0.28	12.0	0.22
522.0 C5 ₂	159.11	Carmel Bed	15.3	0.28	11.3	0.51
GV015	159.17	Carmel Bed	15.6	0.21	10.9	0.12
GV018B _{JA}	159.64	Carmel Bed	14.9	0.24	8.4	1.18
GB005 _N	160.29	Carmel Bed	14.7	0.24	9.6	0.22
GV019	160.36	Carmel Bed	16.1	0.21	11.7	0.30
GV019B _{JA}	160.36	Carmel Bed	15.2	0.24	8.3	0.69
GV047B _{JA}	160.91	Carmel Bed	15.6	0.24	9.2	1.29
GV021B	161.80	Carmel Bed	15.1	0.24	9.7	0.73
GV021	161.80	Carmel Bed	15.2	0.21	11.5	0.19
GV025B _{JA}	163.07	Carmel Bed	15.3	0.24	8.1	1.10
GV031 _N	167.25	Carmel Bed	15.1	0.24	10.2	0.39
GV032	167.76	Carmel Bed	15.8	0.21	10.9	0.36
GV002	154.99	Carmel Vein	12.8	0.21	12.2	0.11
GV003	156.00	Carmel Vein	13.0	0.21	11.4	0.10
GV004	156.24	Carmel Vein	13.0	0.21	10.9	0.08
GV006	156.79	Carmel Vein	14.0	0.21	11.1	0.28
519.5 C1 (GB 001) ₂	158.34	Carmel Vein	15.7	0.08	12.5	0.34
519.5 C2 (GB 001) ₂	158.34	Carmel Vein	15.5	0.10	10.9	0.12
519.5 C3 (GB 001) ₂	158.34	Carmel Vein	15.6	0.37	11.2	0.05
519.5 C4 (GB 001) ₂	158.34	Carmel Vein	15.1	0.10	12.6	0.20
GB001 _{JA}	158.34	Carmel Vein	14.9	0.24	9.1	1.23
GV13L	158.79	Carmel Vein	14.9	0.21	10.4	0.20
GV002 _{JA}	159.11	Carmel Vein	14.7	0.24	7.6	0.47
GV023	162.19	Carmel Vein	15.7	0.21	10.8	0.17
GV024	162.31	Carmel Vein	15.0	0.21	10.6	0.15
GV021-1 _{JA}	162.31	Carmel Vein	15.0	0.24	8.2	0.98
GV025	163.07	Carmel Vein	15.9	0.21	11.3	0.09
GV027 _N	164.10	Carmel Vein	14.6	0.24	10.3	0.49
GV028 _{JA}	165.55	Carmel Vein	15.0	0.24	8.3	0.89
GV030	166.98	Carmel Vein	16.1	0.21	12.8	0.08
GV003 _N	168.14	Carmel Vein	14.5	0.24	10.8	0.69
551.65 C1 ₂	168.14	Carmel Vein	16.0	0.28	10.9	0.07
551.65 C2 ₂	168.14	Carmel Vein	15.1	0.28	10.5	0.32
551.65 C3 ₂	168.14	Carmel Vein	16.1	0.05	7.9	0.06
551.65 C4 ₂	168.14	Carmel Vein	16.0	0.28	10.6	0.35
GV033 _{JA}	168.26	Carmel Vein	15.0	0.24	9.2	0.93
GV034 _{JA6}	168.37	Carmel Vein	14.7	0.22	9.4	0.24
GV036	169.13	Carmel Vein	14.9	0.21	11.5	0.07
GV037 _{JA}	169.77	Carmel Vein	15.5	0.24	10.5	1.31
GV042	172.38	Carmel Vein	15.0	0.21	10.3	0.11
GV044 _{JA}	172.96	Carmel Vein	14.5	0.24	9.0	0.62
GV046	174.70	Carmel Vein	15.3	0.21	11.3	0.17
639.5 C1 ₂	194.92	Carmel Vein	11.1	0.17	11.5	1.27
639.5 C2 ₂	194.92	Carmel Vein	10.1	0.27	10.4	0.20
641.5 C1 ₂	195.53	Carmel Vein	10.9	0.41	12.3	0.16
641.5 C2 ₂	195.53	Carmel Vein	11.1	0.41	11.1	0.26
641.5 C3 ₂	195.53	Carmel Vein	10.6	0.41	11.8	0.55

Table 3 – Isotopic composition of the evaporites in the Paradox Formation. All measurements were collected in November 2014, and all oxygen samples were run in triplicate.

Name	Depth (m)	$\delta^{34}\text{S}$	stdev	$\delta^{18}\text{O}$	stdev
Care Creek 1	243.05	13	0.18	10.5	0.8
Care Creek 1	248.32	13.1	0.18	9.7	0.46
Shafer 1	303.43	12.9	0.18	10.3	0.68
Shafer 1	315.22	12.9	0.18	10.7	0.41
Shafer 1	323.3	12.4	0.18	10.9	0.98
Shafer 1	345.92	12.1	0.18	11.6	0.8
Shafer 1	358.23	11.3	0.18	10.9	0.57
Gibson Dome	417.94	12.3	0.18	12.2	0.56

Table 4 – Isotopic composition of the gypsum hydration water, including the calculated isotopic composition of the mother water. For samples from which no hydration water was extracted, we show the % water. These samples had already dehydrated to anhydrite.

Sample Name	Date Measured	Depth (m)	Formation	δD hydration water	stdv	δD mother water	$\delta^{18}O$ hydration water	stdv	$\delta^{18}O$ mother water	% H ₂ O	Deuterium excess mother water
V22 62.73 Upper	Jan-15	19.12	Entrada Vein	-137.66	0.41	-120.96	-11.01	0.04	-14.95	20.9	-1.35
V22 62.73 Lower	Jan-15	19.12	Entrada Vein	-136.98	0.42	-120.27	-11.08	0.05	-15.02	19.6	-0.12
222.2K	Oct-14	67.73	Entrada Vein	-134.70	0.47	-117.94	-11.02	0.04	-14.96	20.1	1.76
222.84	Oct-14	67.92	Entrada Vein	-136.65	0.30	-119.93	-11.20	0.05	-15.14	20.5	1.18
GV048-227.41	Oct-14	69.31	Entrada Vein	-136.96	0.29	-120.24	-11.18	0.04	-15.12	19.1	0.73
ESS123-250.21	Jan-15	76.26	Entrada Vein	-137.31	0.26	-120.60	-11.21	0.06	-15.15	20.28	0.59
303.5E	Jan-15	92.51	Entrada Vein	-134.39	0.55	-117.62	-10.41	0.15	-14.35	20.5	-2.79
GB001 519.5'	Dec-14	158.34	Carnel Bed	-125.22	0.22	-108.27	-10.11	0.07	-14.06	20.9	4.19
GV010B 519.95	Dec-14	158.48	Carnel Bed	-127.54	0.24	-110.65	-10.76	0.03	-14.70	19.7	6.98
GV011-520.35	Oct-14	158.60	Carnel Vein	-123.73	0.41	-106.76	-9.64	0.03	-13.58	20.4	1.92
GV002 522.0	Dec-14	159.11	Carnel Bed	-126.92	0.42	-110.01	-12.26	0.04	-16.20	20.1	19.56
GV018B 523.75	Dec-14	159.64	Carnel Bed	-120.03	0.35	-102.99	-10.83	0.02	-14.77	20.6	15.19
GB003-525.5	Oct-14	160.17	Carnel Bed							0.5	
GV019B 526.1	Dec-14	160.36	Carnel Bed							1.0	
GV047B 527.91	Dec-14	160.91	Carnel Bed							4.2	
GV021B-530.85	Oct-14	161.80	Carnel Bed							1.0	
GV0244 532.52	Dec-14	162.31	Carnel Vein	-116.15	0.31	-99.03	-12.65	0.04	-16.59	19.6	33.66
GV025B 535.0	Dec-14	163.07	Carnel Bed							4.6	
GV027-538.41	Oct-14	164.11	Carnel Vein	-113.22	0.33	-96.05	-11.72	0.03	-15.65	19.0	29.18
GV028H 593.15	Dec-14	165.55	Carnel Bed	-116.88	0.49	-99.77	-10.70	0.03	-14.64	18.7	17.33
GV031-548.72	Oct-14	167.25	Carnel Vein	-121.28	0.10	-104.26	-11.72	0.02	-15.66	12.8	21.02
GV031-548.72	Oct-14	167.25	Carnel Vein							12.8	
GV003-551.65	Oct-14	168.14	Carnel Vein	-123.95	0.14	-106.99	-10.92	0.04	-14.86	18.8	11.86
GV003 552.03	Dec-14	168.26	Carnel Vein	-123.83	0.23	-106.86	-11.00	0.03	-14.94	20.5	12.65
GV034 552.4'	Dec-14	168.37	Carnel Vein	-124.74	0.25	-107.78	-11.10	0.06	-15.04	20.5	12.51
GV037 557.0	Dec-14	169.77	Carnel Vein	-121.59	0.30	-104.58	-10.06	0.06	-14.01	20.7	7.49
GV038 559.9'	Dec-14	170.66	Carnel Vein	-121.11	0.12	-104.09	-9.41	0.03	-13.36	19.7	2.79
GV044 569.45'	Dec-14	173.57	Carnel Vein	-127.42	0.32	-110.52	-10.51	0.04	-14.45	20.9	5.08
639.5 Carnel	Jan-15	194.92	Carnel Vein	-134.47	0.35	-117.71	-10.51	0.08	-14.45	20.6	0.26
641.5 Carnel	Jan-15	195.53	Carnel Vein	-134.70	0.61	-117.94	-10.70	0.07	-14.64	20.5	-2.79

1060 **Table 5** – Sulfur isotopic composition of disseminated pyrite in the Entrada Sandstone. All samples were measured in July 2013.

Name	Depth(m)	Formation	δ34 S	stdev
V22 62.73	19.12	Entrada	17.24	0.36
73.9E	22.52	Entrada	-47.39	0.21
PG 103E	31.39	Entrada	-9.62	0.21
147E	44.81	Entrada	-16.16	0.21
162.8E	49.62	Entrada	-32.46	0.21
250.7E	76.41	Entrada	-6.13	0.21
299 L	91.14	Entrada	0.52	0.36
299 D	91.14	Entrada	-16.08	2.25
322E	98.15	Entrada	13.11	0.21
392.2E	119.54	Entrada	-3.3	0.21
416E	126.8	Entrada	18.82	0.21
449.9E	137.13	Entrada	2.54	0.21
491.6 D	149.84	Entrada	0.1	0.36