

Determining CO₂ storage potential during miscible CO₂ enhanced oil recovery: Noble gas and stable isotope tracers



Jenna L. Shelton^{a,b,*}, Jennifer C. McIntosh^{a,c}, Andrew G. Hunt^d, Thomas L. Beebe^e, Andrew D. Parker^e, Peter D. Warwick^a, Ronald M. Drake II^f, John E. McCray^b

^a Eastern Energy Resources Science Center, United States Geological Survey, Reston, VA 20192, USA

^b Department of Civil and Environmental Engineering, Colorado School of Mines, Golden, CO 80403, USA

^c Department of Hydrology and Atmospheric Sciences, University of Arizona, Tucson, AZ 85721, USA

^d Crustal Geophysics and Geochemistry Science Center, United States Geological Survey, Denver, CO 80225, USA

^e Whiting Petroleum Corporation, Midland, TX 79701, USA

^f Central Energy Resources Science Center, United States Geological Survey, Denver, CO 80225, USA

ARTICLE INFO

Article history:

Received 15 September 2015

Received in revised form 29 April 2016

Accepted 7 May 2016

Available online 10 June 2016

Keywords:

CO₂ flooding

Incidental CO₂ storage

Geochemical tracers

ABSTRACT

Rising atmospheric carbon dioxide (CO₂) concentrations are fueling anthropogenic climate change. Geologic sequestration of anthropogenic CO₂ in depleted oil reservoirs is one option for reducing CO₂ emissions to the atmosphere while enhancing oil recovery. In order to evaluate the feasibility of using enhanced oil recovery (EOR) sites in the United States for permanent CO₂ storage, an active multi-stage miscible CO₂ flooding project in the Permian Basin (North Ward Estes Field, near Wickett, Texas) was investigated. In addition, two major natural CO₂ reservoirs in the southeastern Paradox Basin (McElmo Dome and Doe Canyon) were also investigated as they provide CO₂ for EOR operations in the Permian Basin. Produced gas and water were collected from three different CO₂ flooding phases (with different start dates) within the North Ward Estes Field to evaluate possible CO₂ storage mechanisms and amounts of total CO₂ retention. McElmo Dome and Doe Canyon were sampled for produced gas to determine the noble gas and stable isotope signature of the original injected EOR gas and to confirm the source of this naturally-occurring CO₂. As expected, the natural CO₂ produced from McElmo Dome and Doe Canyon is a mix of mantle and crustal sources. When comparing CO₂ injection and production rates for the CO₂ floods in the North Ward Estes Field, it appears that CO₂ retention in the reservoir decreased over the course of the three injections, retaining 39%, 49% and 61% of the injected CO₂ for the 2008, 2010, and 2013 projects, respectively, characteristic of maturing CO₂ miscible flood projects. Noble gas isotopic composition of the injected and produced gas for the flood projects suggest no active fractionation, while $\delta^{13}\text{C}-\text{CO}_2$ values suggest no active CO₂ dissolution into formation water, or mineralization. CO₂ volumes capable of dissolving in residual formation fluids were also estimated along with the potential to store pure-phase supercritical CO₂. Using a combination of dissolution trapping and residual trapping, both volumes of CO₂ currently retained in the 2008 and 2013 projects could be justified, suggesting no major leakage is occurring. These subsurface reservoirs, jointly considered, have the capacity to store up to 9 years of CO₂ emissions from an average US powerplant.

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1. Introduction

Miscible carbon dioxide (CO₂) flooding of depleted oil reservoirs, where CO₂ is injected as a supercritical fluid and forms a single phase with the residual crude oil, is being more commonly

applied for enhanced oil recovery (EOR) as primary production from major oil and gas reservoirs in the United States declines. Currently, most of the CO₂ used for EOR comes from natural sources (i.e., non-anthropogenic CO₂). The Permian Basin of Texas and New Mexico is one of the major areas of miscible CO₂ flooding in the United States, and the operations use CO₂ primarily produced from Bravo Dome, McElmo Dome, and Doe Canyon reservoirs (e.g., Hill et al., 2013). To evaluate the future supply of natural CO₂ for EOR operations in the United States, it is important to understand the sources of CO₂ (e.g., mantle or crustal derived) to better understand how CO₂ sup-

* Corresponding author at: Eastern Energy Resources Science Center, United States Geological Survey, Reston, VA 20192, USA.

E-mail address: jlshelton@usgs.gov (J.L. Shelton).

ply may change in the future. These natural CO₂ reservoirs have also been studied as potential geologic CO₂ sequestration analogs (e.g., Lewicki et al., 2007; Gilfillan et al., 2008), as they have stored CO₂ for, potentially, millions of years, and will likely have increased CO₂ storage capacity as the reservoirs are depleted. Additionally, depleted oil reservoirs have been proposed as potential CO₂ sequestration reservoirs, particularly post-EOR operations (e.g., Emberley et al., 2004; White, 2009; Hill et al., 2013). However, limited data currently exists on the possible fates or storage mechanisms of CO₂ during EOR operations; CO₂ could travel outside the production area, dissolve in residual oil and water, or become stratigraphically trapped in the formation (e.g., buoyant or residual trapping) (Hill et al., 2013). If CO₂ migrates out of the target area, this may have negative implications for using these reservoirs for permanent anthropogenic CO₂ storage.

Noble gases are emerging as a useful tool for tracing CO₂ fate and transport in reservoirs used for geologic CO₂ sequestration studies (e.g., Gilfillan and Haszeldine, 2011; Holland and Gilfillan, 2013; Györe et al., 2015), as different sources of natural CO₂ have different noble gas isotopic ratios. For example, non-anthropogenic CO₂ sourced from Bravo Dome has a different noble gas signature than CO₂ sourced from McElmo Dome (Gilfillan et al., 2008). Noble gases have been used mostly as a tracer of CO₂ leakage from a target reservoir, and some research also suggests that noble gases may travel more quickly than CO₂ through subsurface material, making them possible pre-indicators of CO₂ leakage in geologic CO₂ sequestration sites (Cohen et al., 2013; Gilfillan et al., 2014). Noble gases fractionate during various transport and partitioning processes as the system moves away from equilibrium (e.g., Bosch and Mazor, 1988; Zhou et al., 2005; Gilfillan et al., 2008, 2009; Holland and Gilfillan, 2013; Prinzhofer, 2013), and, when combined with other geochemical data, can therefore be used to infer if a reservoir is out of equilibrium and if CO₂ is being stored in a reservoir.

The primary objectives of this study were to: (1) verify the source and establish the geochemical and isotopic signature of the CO₂ produced from Doe Canyon and McElmo Dome (because they are likely the source fields for the CO₂ injected for the sampled EOR projects); and (2) infer if CO₂ storage is occurring during CO₂-miscible EOR, and attempt to quantify the storage amount. Noble gases and natural gas geochemistry were used to track the fate and transport of CO₂ from its determined source, the Paradox Basin of Colorado, to its eventual sink in miscible CO₂ flooding sites in the Permian Basin of Texas. CO₂ gas was sampled from two known sources for Permian Basin EOR operations, McElmo Dome and Doe Canyon in the Paradox Basin, while gas and water were also sampled from four different areas, one waterflood and three miscible CO₂ flood areas in the North Ward Estes Field of the Permian Basin in order to infer possible storage mechanisms for CO₂ in EOR sites.

2. Brief history of McElmo Dome, Doe Canyon, and the North Ward Estes field

McElmo Dome and the adjacent Doe Canyon (Fig. 1) produce CO₂ from the Leadville Limestone, a Mississippian dolomitic carbonate, which occurs between 1800 m and 2600 m below ground surface and has an average thickness of 100 m across the production area (Stevens et al., 2001). CO₂ has been commercially produced from McElmo Dome since 1984, and at that time, the produced gas composition exceeded 98% CO₂ (Stevens et al., 2001). At the time of sampling, the Doe Canyon gas processing facility was being expanded to facilitate additional CO₂ production from the area. Kinder Morgan, LLC, currently operates both fields.

Some work has been performed on the natural CO₂ reservoirs in the greater Colorado Plateau region, mostly to assess the source of the CO₂ (Gilfillan et al., 2008), and the feasibility of using these nat-

ural CO₂ reservoirs for anthropogenic CO₂ storage (Allis et al., 2001; Shipton et al., 2004; Gilfillan et al., 2008). Initially, it was thought that the CO₂ produced from these two fields formed during the thermal breakdown of the carbonate formation (Cappa and Rice, 1995). Gilfillan et al. (2008) sampled natural CO₂-producing wells from both McElmo Dome and Doe Canyon, where they determined that the CO₂ produced from McElmo Dome was mostly mantle derived, as the CO₂/³He ratios from all wells sampled fell between 1×10^9 and 1×10^{10} , the currently accepted magmatic range for CO₂/³He ratios (Marty and Jambon, 1987; Sherwood Lollar et al., 1997; Ballentine et al., 2001). However, a few of the McElmo Dome wells produced gas with relatively high CO₂/³He ratios, in which Gilfillan et al. (2008) concluded that crustal CO₂ might be contributing to McElmo Dome gas. High ²¹Ne/²²Ne ratios and low ²⁰Ne/²²Ne ratios also supported this conclusion. The Doe Canyon sampled gas had a CO₂/³He ratio much lower than the accepted magmatic range, suggesting CO₂ fractionation or loss (Gilfillan et al., 2008).

The EOR projects sampled for this study produce from the Guadalupian (in age) Yates and Queen formations of the North Ward Estes oil field, which lies on the Midland Basin of the larger Permian Basin (Figs. 1 and 2). The Permian Basin began producing oil in the 1920s and currently accounts for roughly 14% of total US oil production (Dutton et al., 2004; Texas Railroad Commission, 2013). The North Ward Estes Field, as of March 2013, is the 11th largest cumulative oil-producing field in the Permian Basin (Texas Railroad Commission, 2013). The Yates and Queen formations are similar: both produce from multiple pay zones and are heterogeneous siliciclastic, transitioning updip to evaporites and red beds (Dutton et al., 2004). The Queen Formation is a mixed shelf clastic carbonate, comprised of mostly dolomite, sandstone, and siltstone, that produces oil, brine and gas from depths between approximately 910 and 1000 m below ground surface (Crandall, 1929; Moran, 1954; Ward et al., 1986). The relatively less productive Seven Rivers Formation is encountered between the Queen and Yates formations, and is approximately 30 m thick. The Yates Formation is a carbonate-siliciclastic unit with varying porosity, permeability, and oil production across the Permian Basin (Borer and Harris, 1991). It produces crude oil, gas and brine from depths between approximately 730 and 880 m below the surface (Dutton et al., 2004).

Whiting Petroleum Corporation currently operates the North Ward Estes Field. The field was discovered in 1929, produces from a surface area of approximately 1.6×10^8 m² (39,000 acres), and was estimated to contain approximately 1.3×10^{11} L (1.1 billion barrels) of original oil in place (OOIP) (Ring and Smith, 1999). As of November 2013, the North Ward Estes Field contained more than eight CO₂ flood expansion areas and/or miscible CO₂ floods, either in the pre-EOR phase (primary production supported by waterflood operations), or supporting water-alternating-gas (WAG) operations. Miscible CO₂ flooding via WAG is currently being applied across the North Ward Estes Field, with 100% of the CO₂ coming from the Cortez pipeline (Fig. 1).

3. Methods

A total of 18 different locations were sampled in November of 2013 for this study (Fig. 1; Table 1). They included injection wells, production wells, satellite stations (areas where produced water, oil and gas from numerous wells are initially piped and combined into one larger mixture), and processing plants (CO₂ purification and compression plants) (Fig. 1; Table 1). Three produced gas and water samples were collected from three CO₂ processing areas in the McElmo Dome CO₂ field. The processing plants allowed for the sampling of co-mingled Leadville Formation gas from various production wells. The three processing stations at McElmo Dome will

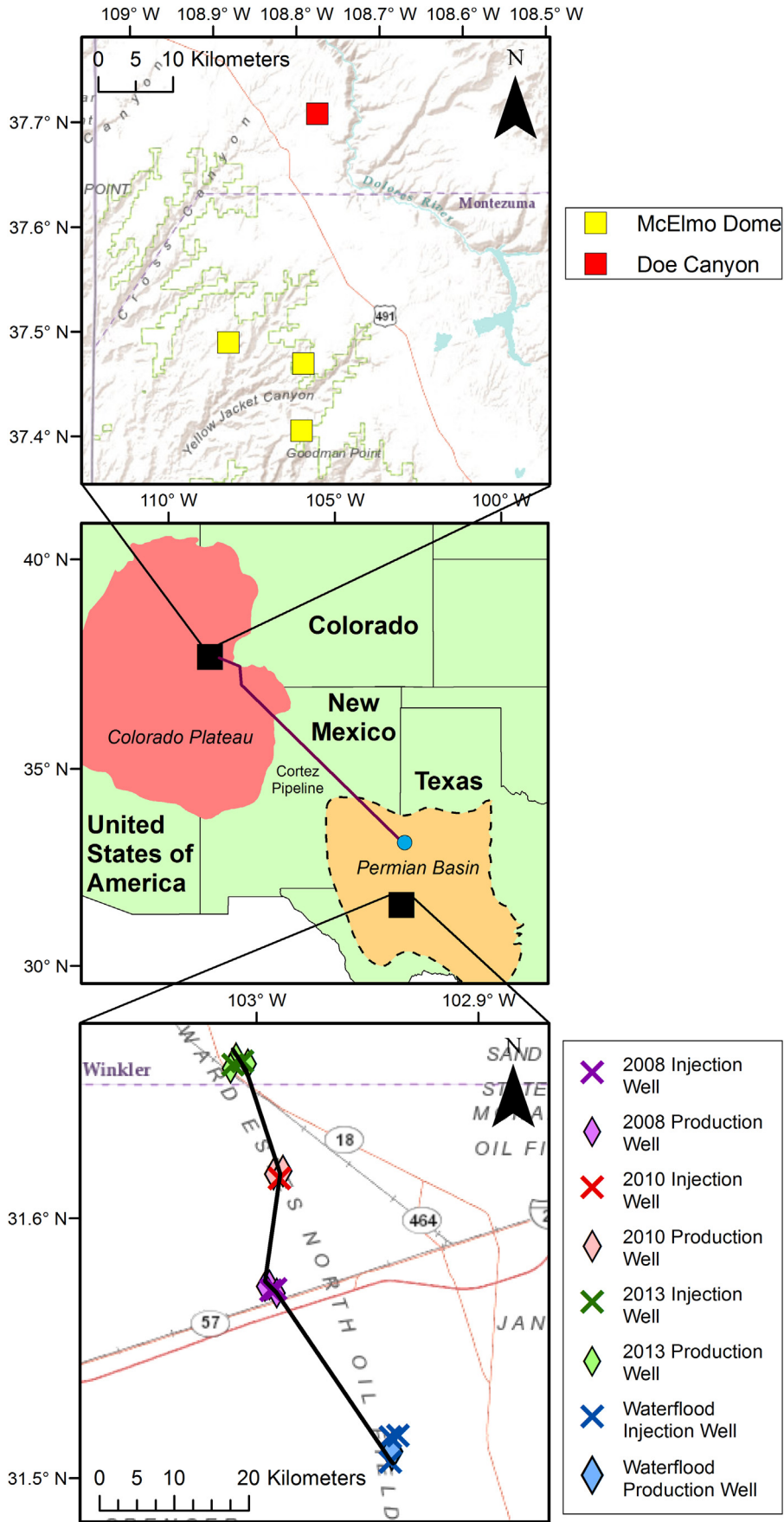


Fig. 1. Locations of the sampled areas for this study. The upper map of Colorado shows locations of the four CO₂ processing facilities sampled; the lower map of Texas shows wells sampled in the North Ward Estes Field near Wickett, Texas. The middle map shows the location of the Colorado Plateau (Fenneman and Johnson, 1946), and

be identified heretofore as simply “McElmo Dome.” One produced gas sample was collected from the Doe Canyon CO₂ processing plant.

Four different post-primary recovery project phases in the North Ward Estes Field in Texas were also sampled; three projects under a miscible CO₂ flood and one under a waterflood (pre-CO₂ injection). The wells in each project area were chosen due to their proximal surficial location – within the same 5 spot pattern (one injection well located at the center of a 4 corner square of producing wells) or line drive (injection wells are parallel to production wells, both forming a straight line)– and their stratigraphic positions (i.e., which sands the wells were drilled into; Fig. 2) so that the chosen wells were likely in communication with each other. The waterflood area was used as an analogue for pre-CO₂ injection geochemical conditions for the current CO₂ flooded areas, as the sites share similar lithology and therefore, hydrogeochemical changes due to CO₂ flooding operations may be discerned. The different EOR projects are identified in this study by their project start dates, which were 2008, 2010, and 2013, whereas the single waterflooded area is identified as “Waterflood.” The sampling and analysis methods for each of the sites are described below.

The McElmo Dome and Doe Canyon CO₂ processing facilities allowed for gas sampling before processing, compression and distribution into the Cortex pipeline that connects to the Permian Basin. Isotech[®] gas canisters were attached to outlet points along the CO₂ inlet pipeline, and flushed for 10 s 10 times before sample collection. An Isotech[®] Gas Sampling Manifold was then attached to the gas outlet point, and one end of Nalgene PVC tubing was attached to the sampling port of the Manifold. The other end of the PVC tubing was attached to one end of a 20 mm long piece of refrigeration grade copper tubing. The outlet-end of the copper tube was attached to another length of Nalgene tubing, with the end of the tubing placed in a beaker of Milli-Q water to prevent atmospheric gas back-flow into the copper tube. The Isotech[®] Gas Sampling Manifold kept the inflow pressure below 100 psi, and the copper tube apparatus was flushed for at least 30 s. The gas line was shutoff, and the inlet end of the copper tube was cold welded shut, followed by the outlet end (this allowed for the final gas pressure in the tube to be at atmospheric pressure). The Isotech[®] canisters were shipped to Isotech[®] Laboratories in Champaign, Illinois for gas composition and compound-specific isotope analysis, and the copper tubes were transported to the U.S. Geological Survey Noble Gas Laboratory in Lakewood, Colorado, for gas composition (including noble gases) and isotopic analysis.

The four EOR project phases (3CO₂ floods and 1 waterflood) in the North Ward Estes Field were sampled for produced gas and water, and injected gas and water. Injected and produced gas were collected from the wellhead in Isotech[®] Isotubes[®] (attached to the Isotech[®] Gas Sampling Manifold) that were flushed for at least 20 s three times prior to sample collection. The Isotubes[®] were shipped to Isotech[®] Laboratories for gas composition and compound specific isotope analysis. Noble gases were also collected via the copper tube method discussed above, and transported to the U.S. Geological Survey Noble Gas Laboratory.

Due to the dramatic drop in temperature that occurs when pressurized CO₂ is brought from reservoir conditions (supercritical fluid) to atmospheric pressure, produced water could not be sampled at the wellhead (as it was produced as a frozen slush). Therefore, produced water was collected at satellite stations. It is important to note that although the water was collected at satel-

lite stations, which mix fluids from multiple adjacent wells into one larger stream, we were able to sample fluids from individual wells before fluid combination. This produced water was collected in 1-gallon (3.78 L) plastic jugs from an outlet port, filtered through 0.2 μm nylon syringe filters attached to 60 mL sterile BD syringes into a 30 mL HDPE bottle, and placed on ice until analysis. We collected injected water at the wellhead (as it was not frozen), following the same procedure as was used for the produced water.

Alkalinity for both the injected and produced North Ward Estes Field waters was titrated within 8 h of sample collection using the Gran-Alk method (Gieskes and Rogers, 1973; McIntosh et al., 2004; McIntosh et al., 2010), while pH was determined in the field using a pH/conductivity meter and an Orion conductivity probe, calibrated daily. Temperature of the produced North Ward Estes Field fluids could not be determined due to the samples being collected at satellite stations. Bulk gas concentrations were measured on a quadrupole MS in U.S. Geological Survey the Noble Gas Laboratory in Lakewood, Colorado, and at Isotech Laboratories in Champaign, Illinois. Stable isotopes of hydrocarbons and CO₂ (δ¹³C–CO₂, δ¹³C–CH₄, δ¹³C-ethane, δ¹³C-propane) were analyzed via gas chromatography combustion isotope ratio mass spectrometry (GC–C-IRMS; precision ±0.3‰) while δ²H–CH₄ was analyzed via gas chromatography pyrolysis isotope ratio mass spectrometry (GC–P-IRMS; precision ±5.0‰) by Isotech[®] Laboratories of Champaign, Illinois (Table 2).

For noble gas analyses, a cold welded copper tube containing a gas sample was attached to an ultra-low vacuum extraction line pumped down to a pressure less than 1.3×10^{-11} MPa. The copper tube was then opened and the sample gas expanded through two co-axial dry ice ethanol traps (~200 K), and flowed into the extraction line. The sample gas was exposed to an aluminum zirconium trap at 632 K to remove the reactive gases, producing a homogenized noble gas fraction sample. Argon, krypton and xenon isotopes were measured on a MAP 215-50 magnetic sector mass spectrometer. To separate the helium and neon fractions from the argon-krypton-xenon components, the remaining sample was exposed to successive cryogenic traps (LN₂/charcoal and helium cryostat). The helium and neon fractions were successively released from the cryostat and measured on the MAP 215-50 for quantitative isotopic compositions. Data for the calculation of isotopic compositions were compiled from calibration curves from successive aliquots of an in-house air standard. Reported errors, ranging from 0.5% to 6.61% for the noble gas concentrations, represent the reproducibility of the air standards to the generated calibration curves (Hunt et al., 2013).

4. Results

The analytical results for the 18 samples collected in November 2013 for this study are outlined in Tables 1–3: Table 1 provides sample location information; Table 2 provides pH, alkalinity, molecular and isotopic composition data for the gases and waters collected; and Table 3 provides isotopic ratio information for noble gases.

4.1. Gas geochemistry of McElmo Dome and Doe Canyon

Concentrations of the major geochemical elements (e.g., CH₄, CO₂, He) of the gas produced from the three processing stations of McElmo Dome were all similar (Table 2). The CO₂ content for McElmo Dome produced gas averaged 98.2 mol%, with nitrogen

Table 1
Sample Information.

API Number/Processing Plant	Sample Date	Well Type	Phase/Flood Start	Total Gas Injected or Produced (at STP as of November 2013) (m ³)	CO ₂ Injected or Produced (at STP as of November 2013) (m ³)	Producing Formation and Sand	County and State	Latitude	Longitude	Production Depth (m below sea level)
EOR 2008										
424750159700	November 12, 2013	Injection (CO ₂)	Phase 1, January 2008	7.3 × 10 ⁹	7.1 × 10 ⁹	Yates Strays	Ward, Texas	31.572340	−102.993500	800
424751026600	November 12, 2013	Injection (CO ₂)	Phase 1, January 2008			Yates J1	Ward, Texas	31.572863	−102.991470	825
424751117800	November 12, 2013	Production	Phase 1, January 2008	4.4 × 10 ⁹	4.3 × 10 ⁹	Yates J2	Ward, Texas	31.574326	−102.994252	833
424750159000	November 12, 2013	Production	Phase 1, January 2008			Yates Strays	Ward, Texas	31.573778	−102.996298	794
424750162300	November 12, 2013	Production	Phase 1, January 2008			Yates J2	Ward, Texas	31.571233	−102.990968	831
EOR 2013										
424951100400	November 12, 2013	Injection (CO ₂)	Phase 3C, April 2013	7.2 × 10 ⁷	7.0 × 10 ⁷	Yates J3	Winkler, Texas	31.660367	−103.006388	853
424951100200	November 12, 2013	Injection (CO ₂)	Phase 3C, April 2013			Yates J3	Winkler, Texas	31.659155	−103.010653	874
424953172200	November 12, 2013	Production	Phase 3C, April 2013	2.8 × 10 ⁷	2.7 × 10 ⁷	Yates J1	Winkler, Texas	31.659316	−103.003843	824
424953113600	November 12, 2013	Production	Phase 3C, April 2013			Yates J3	Winkler, Texas	31.661650	−103.009283	863
424953167200	November 12, 2013	Production	Phase 3C, April 2013			Yates J3	Winkler, Texas	31.657541	−103.011706	880
EOR 2010										
424750225101	November 12, 2013	Injection (CO ₂)	Pilot Phase 2, January 2010	6.3 × 10 ⁸	6.1 × 10 ⁸	Queen Q6	Ward, Texas	31.615385	−102.989723	996
424753034100	November 12, 2013	Production	Pilot Phase 2, January 2010	3.4 × 10 ⁸	3.1 × 10 ⁸	Queen Q5	Ward, Texas	31.617083	−102.992433	983
424753344900	November 12, 2013	Production	Pilot Phase 2, January 2010			Queen Q6	Ward, Texas	31.618213	−102.988175	992
Waterflood										
424750249800	November 13, 2013	Gas Production	Phase 8A, April 2009	n/a	n/a	Yates A	Ward, Texas	31.516502	−102.936273	749
424753495500	November 13, 2013	Water Production	Phase 8A, April 2009	n/a	n/a	Yates D	Ward, Texas	31.506360	−102.939710	778
424753048100	November 13, 2013	Water Production	Phase 8A, April 2009	n/a	n/a	Yates Q	Ward, Texas	31.515930	−102.939710	968
424753491100	November 13, 2013	Water Injector	Phase 8A, April 2009	n/a	n/a	Yates Q	Ward, Texas	31.510340	−102.939020	974
McElmo Dome										
Goodman Point	November 6, 2013	Processing Facility	n/a	n/a	n/a	Leadville	Montezuma, Colorado	37.405474	−108.793350	n/a
Yellow Jacket	November 6, 2013	Processing Facility	n/a	n/a	n/a	Leadville	Montezuma, Colorado	37.469698	−108.791226	n/a
Hovenweep	November 6, 2013	Processing Facility	n/a	n/a	n/a	Leadville	Montezuma, Colorado	37.489876	−108.881358	n/a
Doe Canyon										
Doe Canyon	November 6, 2013	Processing Facility	n/a	n/a	n/a	Leadville	Dolores, Colorado	37.708193	−108.774455	n/a

n/a indicates the information is not applicable or not available.

Table 2
Gas Geochemistry and Isotopic Ratios.

Well Type	pH	Alkalinity meq/kg	\sim CO ₂ mol%	**CO ₂ cm ³ STP/cm ³	N ₂ mol%	CH ₄ mol%	ΣC ₂₊ mol%	He mol%	Ar mol%	O ₂ mol%	⁴ He cm ³ STP/cm ³ (x10 ⁻⁶)	²⁰ Ne cm ³ STP/cm ³ (x10 ⁻⁶)	³⁶ Ar cm ³ STP/cm ³ (x10 ⁻⁶)	⁴⁰ Ar cm ³ STP/cm ³ (x10 ⁻⁶)	⁸⁴ Kr cm ³ STP/cm ³ (x10 ⁻⁹)	¹³² Xe cm ³ STP/cm ³ (x10 ⁻⁹)	δ ¹³ C—CO ₂ ‰	δ ¹³ C—CH ₄ ‰	δ ¹³ C—C ₂ H ₆ ‰	δ ¹³ C—C ₃ H ₈ ‰	δ ² H—CH ₄ ‰
EOR 2008																					
CO ₂ Injector	-	-	97.8	98.3	1.08	0.50	0.47	0.10	0.02	0.04	1550	0.004	0.025	190	2.22	0.136	-4.4	nd	nd	nd	nd
CO ₂ Injector	-	-	97.7	98.0	1.13	0.53	0.47	0.10	0.02	0.04	1482	0.006	0.029	180	1.92	0.130	-4.4	nd	nd	nd	nd
Producer	7.5	23.5	97.0	97.4	1.34	0.68	0.80	0.11	0.02	0.05	1449	0.004	0.026	191	1.70	0.175	-4.3	nd	nd	nd	nd
Producer	7.5	24.0	97.0	97.2	1.30	0.66	0.87	0.11	0.02	0.04	1406	0.003	0.025	190	1.38	0.132	-4.4	nd	nd	nd	nd
Producer	7.7	22.9	96.7	96.9	1.50	0.73	0.87	0.10	0.02	0.04	1378	0.003	0.026	204	2.02	0.196	-4.4	nd	nd	nd	nd
EOR 2013																					
CO ₂ Injector	-	-	97.5	98.1	1.26	0.56	0.49	0.11	0.02	0.07	1335	0.003	0.021	163	1.34	0.140	-4.4	nd	nd	nd	nd
CO ₂ Injector	-	-	97.8	96.6	1.06	0.50	0.48	0.10	0.02	0.04	1380	0.005	0.027	175	1.91	0.129	-4.5	nd	nd	nd	nd
Producer	-	-	96.7	97.6	1.30	0.75	1.10	0.11	0.02	0.05	1461	0.004	0.024	184	1.75	0.145	-4.5	nd	nd	nd	-207.9
Producer	7.3	12.7	96.3	95.9	1.34	0.91	1.24	0.11	0.02	0.06	1516	0.004	0.026	187	1.62	0.144	-4.4	nd	nd	nd	-199.9
Producer	7.3	12.6	96.2	97.4	1.27	1.06	1.27	0.12	0.02	0.03	1520	0.003	0.024	186	1.86	0.150	-4.5	nd	nd	nd	nd
EOR 2010																					
CO ₂ Injector	-	-	97.5	-	1.24	0.57	0.50	0.11	0.02	0.04	-	-	-	-	-	-	-4.4	nd	nd	nd	nd
Producer	7.6	23.9	89.5	-	1.37	5.40	3.58	0.11	0.02	0.02	-	-	-	-	-	-	-4.3	-53.5	-38.9	-32.1	-221.2
Producer	7.9	41.6	91.3	-	1.42	2.95	4.22	0.11	0.02	nd	-	-	-	-	-	-	-4.5	-53.2	-38.5	-32.1	-212.3
Waterflood																					
Gas Producer	-	-	2.2	1.7	1.31	64.80	31.66	0.01	0.01	0.01	132	0.040	0.210	74	8.78	1.294	-14.1	-50.5	-37.5	-31.9	-219.0
Water Producer	7.7	7.8	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	nd	nd	nd	nd
Water Producer	7.8	7.3	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	nd	nd	nd	nd
Water Injector	7.5	24.1	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	nd	nd	nd	nd
McElmo Dome																					
Processing Facility	-	-	98.2	98.0	1.55	0.11	0.01	0.08	0.02	nd	1001	0.006	0.027	206	2.03	0.158	-4.3	nd	nd	nd	nd
Processing Facility	-	-	98.2	97.9	1.58	0.13	0.01	0.07	0.02	nd	982	0.004	0.025	202	1.46	0.105	-4.4	nd	nd	nd	nd
Processing Facility	-	-	98.2	98.4	1.58	0.14	0.01	0.07	0.02	nd	1023	0.003	0.024	198	2.04	0.154	-4.5	nd	nd	nd	nd
Doe Canyon																					
Processing Facility	-	-	95.3	94.9	3.36	0.92	0.02	0.35	0.04	nd	4547	0.018	0.055	441	4.98	0.261	-4.6	-28.36	nd	nd	-144.1

- indicates that the sample was unavailable.

nd indicates the element was not detected.

\sim CO₂ values used for retention calculations.

**CO₂ values used for noble gas calculations.

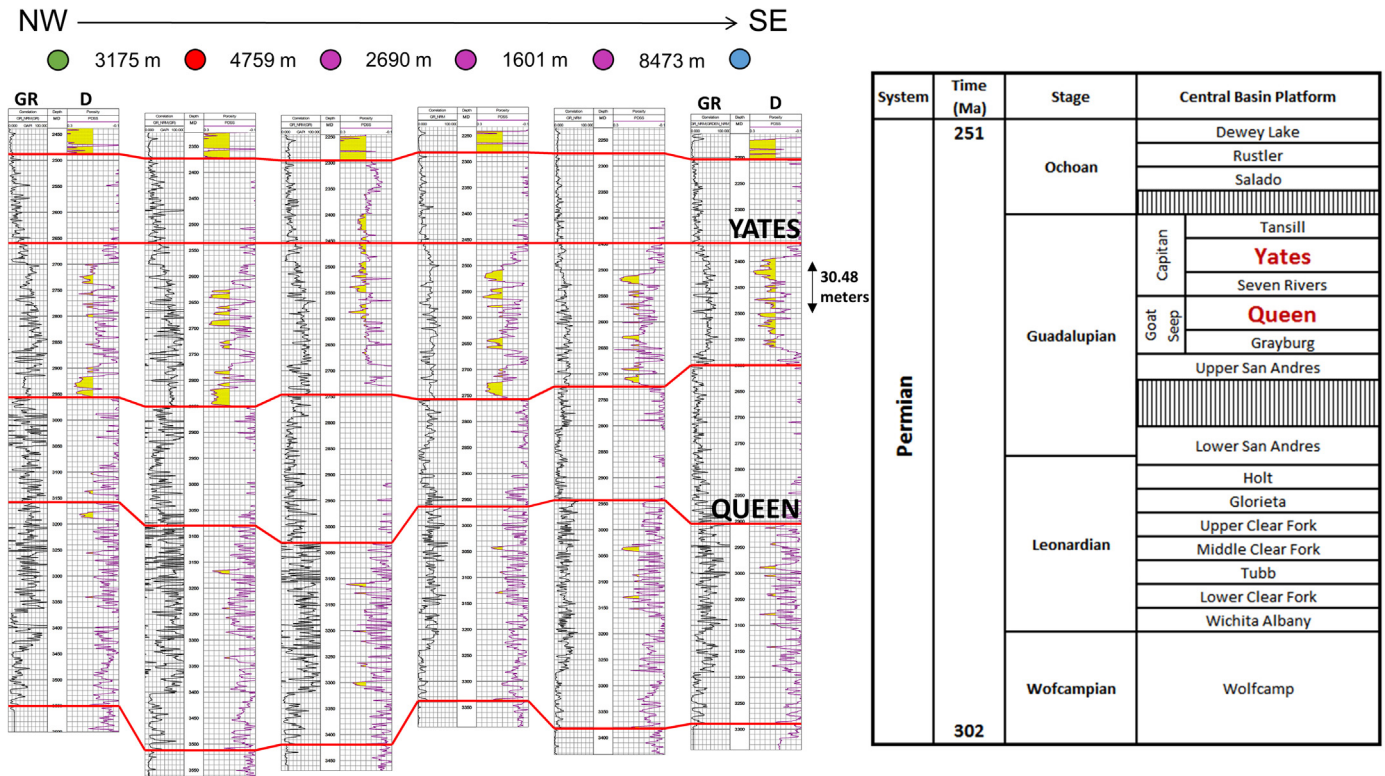


Fig. 2. Well logs for six wells sampled in the North Ward Estes Field. Each log consists of Gamma Ray (GR; left side) and density porosity (D; right side) measurements. The top of the Yates and Queen formations are labeled, and a stratigraphic column is presented on the right. The cross section extends from northeast to southwest across the field, and follows the transect outlined on Fig. 1. The dots correspond to well locations in the North Ward Estes Field (with colors correlating to Fig. 1); distances between wells are indicated on the top of the figure. Well logs provided by Whiting Petroleum; stratigraphic column modified from Dutton et al. (2004).

Table 3
Noble Gas Isotopic Ratios.

Well Type	CO ₂ / ³ He	³ R/R _A	⁴ He/ ²⁰ Ne (x air)	²⁰ Ne/ ²² Ne	²¹ Ne/ ²² Ne	³⁸ Ar/ ³⁶ Ar	⁴⁰ Ar/ ³⁶ Ar	⁸⁶ Kr/ ⁸⁴ Kr	¹³⁰ Xe/ ¹³² Xe
EOR 2008									
CO ₂ Injector	3.62E+09	0.127	4.14E+05	9.00	0.097	0.179	7645	0.289	0.180
CO ₂ Injector	3.73E+09	0.128	2.66E+05	9.23	0.073	0.180	6326	0.286	0.165
Producer	3.73E+09	0.131	3.81E+05	9.03	0.097	0.180	7328	0.346	0.184
Producer	3.74E+09	0.134	4.16E+05	8.89	0.102	0.180	7710	0.388	0.084
Producer	3.83E+09	0.133	4.12E+05	8.87	0.106	0.185	7710	0.330	0.159
EOR 2013									
CO ₂ Injector	4.23E+09	0.126	4.26E+05	8.88	0.101	0.180	7720	0.347	0.134
CO ₂ Injector	3.94E+09	0.129	4.59E+05	8.96	0.102	0.182	7665	0.322	0.147
Producer	3.70E+09	0.131	4.12E+05	9.11	0.099	0.182	7606	0.317	0.184
Producer	3.54E+09	0.129	4.26E+05	9.05	0.101	0.183	7171	0.378	0.145
Producer	3.70E+09	0.125	2.72E+05	9.29	0.078	0.180	6413	0.325	0.162
EOR 2010									
CO ₂ Injector	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a
Producer	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a
Producer	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a
EOR Waterflood									
Gas Producer	7.31E+08	0.126	3.29E+03	9.79	0.320	0.177	355	0.325	0.143
McElmo Dome									
Processing Facility	4.41E+09	0.155	3.00E+05	9.03	0.108	0.187	8347	0.328	0.189
Processing Facility	4.51E+09	0.161	1.60E+05	9.32	0.072	0.180	7735	0.342	0.170
Processing Facility	4.41E+09	0.164	2.80E+05	9.13	0.101	0.181	8157	0.333	0.125
Doe Canyon									
Processing Facility	2.00E+09	0.076	2.57E+05	9.17	0.062	0.176	7986	0.335	0.170

* R is the ³He/⁴He ratio of the sample, while R_A is the ³He/⁴He ratio of the atmosphere, equal to 1.384 × 10⁻⁶ (Clarke et al., 1976).

being the next greatest component (1.57 mol% average). CO₂/³He ratios for McElmo Dome ranged from 4.4 × 10⁹ to 4.5 × 10⁹, R/R_A (³He_{sample}/⁴He_{sample} to ³He_{air}/⁴He_{air}) ranged from 0.155 to 0.164, and ⁴⁰Ar/³⁶Ar ratios ranged from 7734 to 8347 (Table 3). The

²⁰Ne/²²Ne ratios for gases sampled from McElmo Dome ranged from 9.03 to 9.32, and ²¹Ne/²²Ne ratios ranged from 0.072 to 0.108 (Table 3).

Doe Canyon major element gas geochemistry was slightly different than McElmo Dome gas geochemistry, with CO₂ content being 95.3 mol%; the second largest chemical constituent was also nitrogen, but higher at 3.36 mol%. The CO₂/³He ratio for Doe Canyon was 2.0×10^9 , the R/R_A was 0.076, and the ⁴⁰Ar/³⁶Ar ratio was 7986 (Table 3). The ²⁰Ne/²²Ne ratio for gas sampled at Doe Canyon was 9.17, while the ²¹Ne/²²Ne ratio for Doe Canyon gas was 0.062.

4.2. Injected and produced gas and water geochemistry of the North Ward Estes field

Gas and water are both injected and produced in the North Ward Estes Field, at varying rates and with varying geochemistry. Supercritical fluid (mostly CO₂) has been injected at varying rates throughout the lifetimes of the EOR three project phases (no gas had been injected into the Waterflood project as of November 2013); the total volume of gas injected into the three EOR project phases over their respective lifetimes were 7.3×10^9 m³, 6.3×10^8 m³, and 7.2×10^7 m³ for the 2008, 2010, and 2013 project phases, respectively (Table 1). The injected fluid for the 2008 project phase is composed of mostly CO₂, at an average of 97.8 mol%, with nitrogen being the next largest geochemical component, at 1.08 mol% (Table 2). The 2010 and 2013 EOR project phases also injected fluid that was mostly CO₂, averaging 97.7 mol% and 97.5 mol%, respectively, with nitrogen also being the second most abundant chemical constituent (Table 2). The δ¹³C–CO₂ value for the 2008 injected fluid averages –4.4‰, the ⁴He content averages 1.5×10^{-3} cm³STP/cm³, the CO₂/³He ratio averages 3.7×10^9 , and the R/R_A averages 0.128 (Tables 2 and 3). The δ¹³C–CO₂ value for the 2010 injected fluid also averages –4.4‰ (Table 2), while no noble gas geochemistry could be analyzed, due to the copper sample collection tubes rupturing post-collection. The δ¹³C–CO₂ value for the 2013 injected fluid averages –4.4‰, the ⁴He content averages 1.4×10^{-3} cm³STP/cm³, the CO₂/³He ratio averages 4.1×10^9 , and the R/R_A averages 0.128 (Tables 2 and 3). Water is constantly injected into the Waterflood project (the other 3 project phases are water-alternating-gas injections); the alkalinity of the injected water is 24.1 meq/kg, while the pH is 7.5.

Total gas produced from the three EOR project phases over their respective lifetimes vary geochemically; total gas production volumes as of November 2013, are 4.4×10^9 m³, 3.4×10^8 m³, and 2.8×10^7 m³ for the 2008, 2010, 2013 projects, respectively. The 2008 project phase produced gas is composed of mostly CO₂, but at a lower mol% than the injected gas, averaging 96.9 mol%, (Table 2). The 2010 and 2013 EOR project phases also produce mostly CO₂ at lower concentrations than that injected into each project, at average concentrations of 90.4 mol% and 96.4 mol%, respectively. Produced gas for all three project phases produce the same average δ¹³C–CO₂ value as is injected, –4.4‰, –4.4‰, and –4.5‰ for the 2008, 2010, and 2013 project phases, respectively. The Waterflood produces gas with a δ¹³C–CO₂ value of –14.1‰ (Table 2). The ⁴He content for the 2008 produced gas averages 1.4×10^{-3} cm³STP/cm³, the CO₂/³He ratio averages 3.8×10^9 , and the R/R_A ratio averages 0.133 (Tables 2 and 3). The ⁴He content for the 2013 EOR project phase averages 1.5×10^{-3} cm³STP/cm³, the CO₂/³He ratio averages 3.6×10^9 , and the R/R_A ratio averages 0.128 (Tables 2 and 3). Again, the noble gas geochemistry was not analyzed for the 2010 project due to faulty gas collection equipment.

Water is co-produced (along with oil and gas) from all four project phases. The pH averages 7.5, 7.8, 7.3, and 7.8 for the 2008, 2010, 2013 EOR project phases, and Waterflood project, respectively. The alkalinity averages 23.5 meq/kg, 32.8 meq/kg, 12.7 meq/kg, and 7.6 meq/kg for the 2008, 2010, 2013 EOR project phases, and Waterflood project, respectively. Temperature of the formation water could not be determined because the fluid was produced as a slush, caused by the pressure drop of the CO₂ as

it reaches the surface. However, the average reservoir temperature for the four sampled reservoirs is approximately 28 °C (written communication, Whiting Petroleum Corporation, 2014). The produced water chemistry from the Waterflood project phase likely reflects pre-CO₂ injection water geochemistry for the 2008 and 2013 projects, as no CO₂ had been injected into the target sand at the time of sample collection.

5. Discussion

5.1. Defining the geochemistry and source of the natural CO₂ of the Paradox Basin

Traditionally, δ¹³C–CO₂, R/R_A values, ²⁰Ne/²²Ne ratios, ²¹Ne/²²Ne ratios and ⁴⁰Ar/³⁶Ar ratios have been used as diagnostic tools to determine mantle, air, and crustal components to natural gases, and there are recognized values for the four ratios for each (e.g., mantle, crustal) gas source (e.g., crustal ²⁰Ne/²²Ne equals 9.7, mantle ²⁰Ne/²²Ne equals 12.5, air ²⁰Ne/²²Ne equals 9.8; Mamyrin et al., 1970; Graham, 2002; Ozima and Podosek, 2002; Holland and Ballentine, 2006; Lee et al., 2006; Valkiers et al., 2010). Previous research focusing on McElmo Dome and Doe Canyon fields suggest varying sources for the CO₂ produced. Gilfillan et al. (2008) used CO₂/³He ratios and CO₂ content as evidence for a magmatic source for the CO₂ produced from McElmo Dome and Doe Canyon (Fig. 2A). Karlstrom et al. (2013) also suggested a mantle source for various natural geothermal and carbonic springs throughout the Rocky Mountain region, relying mostly on R/R_A values. Adams et al. (2015) suggested a mixed mantle–crustal gas source for these two CO₂ fields, using a combination of gas composition data, noble gas concentrations, and stable isotope signatures.

The gas analyzed from McElmo Dome and Doe Canyon is geochemically similar to the gases previously sampled in the study area (Gilfillan et al., 2008; Adams et al., 2015). The δ¹³C–CO₂ values and corresponding CO₂ content of the gas collected from McElmo Dome and Doe Canyon for this study suggest either alteration of marine carbonates or magmatic/volcanic sources for the produced CO₂ (e.g., Holland and Gilfillan, 2013). CO₂ content and CO₂/³He ratios plot similarly to data collected by Gilfillan et al. (2008), also suggesting a mantle source for the CO₂ gas (Fig. 3A). However, the noble gases do not suggest a mantle-derived source.

Using argon isotope ratios and R/R_A values (Fig. 3B), it appears that the noble gases from McElmo Dome and Doe Canyon are mostly crustal in origin, with all gases falling within the accepted range for crustal ⁴⁰Ar/³⁶Ar ratios. The R/R_A values for McElmo Dome suggest mixing with either the air, likely due to mixing with air saturated water or formation water, or mantle gas sources, as the R/R_A values are larger than 0.1. Doe Canyon gas geochemistry agrees with the ⁴⁰Ar/³⁶Ar diagnostic, being less than 0.1 and suggesting a crustal origin. When examining the ²⁰Ne/²²Ne and ²¹Ne/²²Ne values, the isotopic values suggest a different source (Fig. 3C). Both neon isotope ratios plot closest to the air endmember (with no other gas composition evidence of actual air contamination), with likely contributions from both the mantle and the crust. This is likely caused by gas-formation water interactions (Gilfillan et al., 2008, 2009), and not by actual air addition into the system. Generally, ²⁰Ne/²²Ne and ²¹Ne/²²Ne values for McElmo Dome and Doe Canyon suggest a greater atmospheric contribution when compared to Gilfillan et al. (2008), as gases sampled for this study are shifted towards the air endmember, suggesting gas/water partitioning. These data suggest that the bulk gas contribution (i.e., CO₂) is likely sourced from the mantle. However, some of the bulk gas contribution may be sourced from the crust, as the noble gas data suggest.

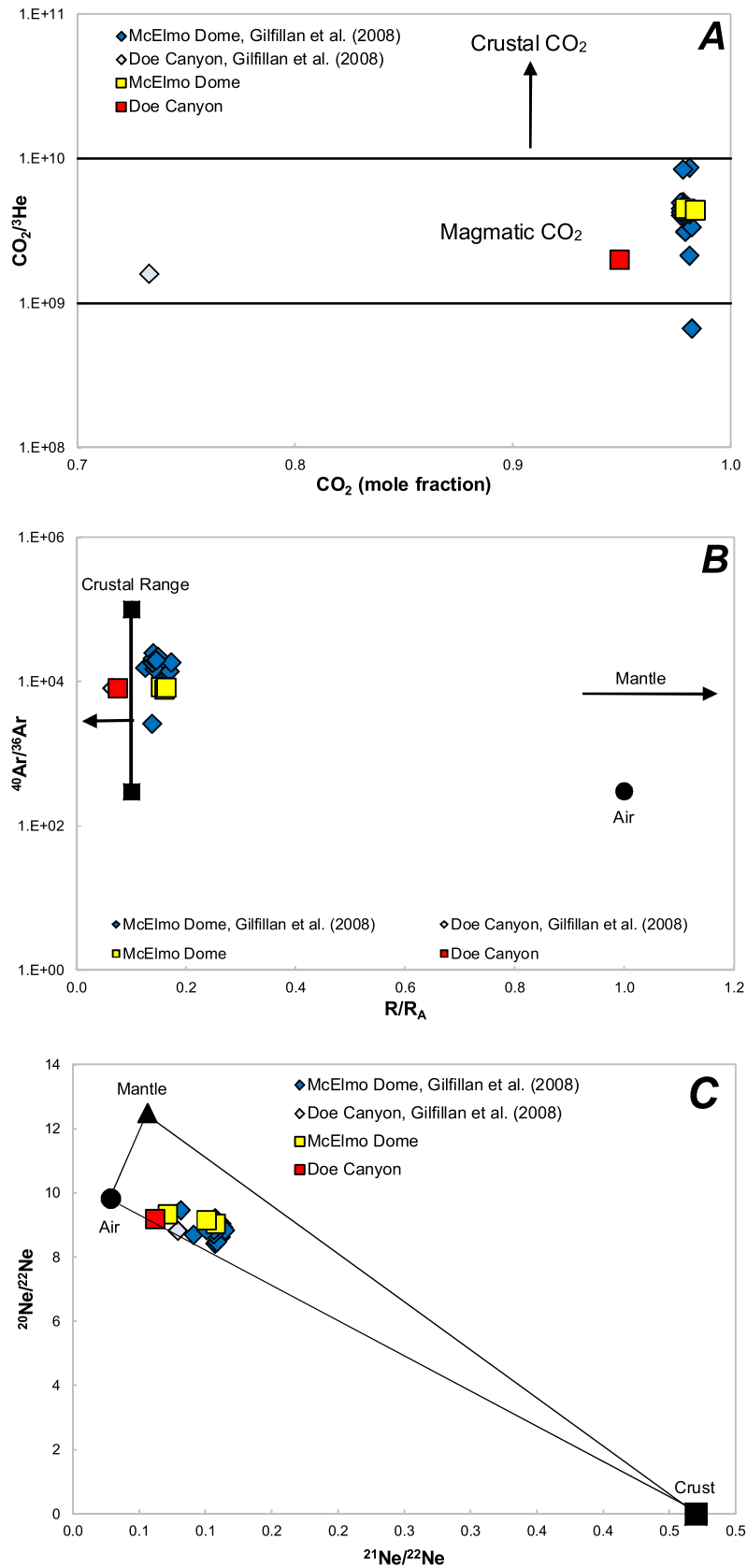


Fig. 3. McElmo Dome and Doe Canyon noble gas data from this study and from Gilfillan et al. (2008). $CO_2/{}^3He$ and CO_2 content (A): this study shows a much tighter range for $CO_2/{}^3He$ ratios, and generally a higher CO_2 content for corresponding sites, with data plotting in mainly the magmatic range for $CO_2/{}^3He$. The 'Magmatic CO_2 ' label signifies the $CO_2/{}^3He$ range between 1×10^9 and 1×10^{10} , while the 'Crustal CO_2 ' label signifies any $CO_2/{}^3He$ ratio larger than 1×10^{10} . Argon and helium isotopes (B): data for this study is similar to data collected by Gilfillan et al. (2008), and generally indicates a crustal source for the gas produced, with either a slight air or mantle (endmember located off of the graph) component. The arrow to the left of the crustal line indicates that crustal CO_2 values for R/R_A values can also plot to the left of the line. Neon isotopes (C): generally, gases collected for this study have similar ${}^{21}Ne/{}^{22}Ne$ and ${}^{20}Ne/{}^{22}Ne$ ratios when compared to Gilfillan et al. (2008), while the isotopic ratios suggest air-crust mixing as a source for the gas.

5.2. Determining volumes of CO₂ incidental storage in the North Ward Estes field

To determine natural CO₂ geochemistry changes from source to sink in an EOR field, we sampled the North Ward Estes oil field, which is currently undergoing a multi-phase miscible CO₂ flood EOR project. The non-recycled (i.e., purchased) CO₂ injected into the North Ward Estes Field is piped from the Denver City Hub (Fig. 1). Due to the likelihood of miscible CO₂ flood reservoirs to be sinks for injected CO₂, the injection and production rates of gas for 3 different CO₂ flood projects in the North Ward Estes Field were used to determine the amount of CO₂ that is currently being retained in the subsurface for each miscible CO₂ flood project (i.e., incidentally stored).

If the total gas injection and production rates (coupled with the CO₂ mol% of the produced gas) are known, the percent of CO₂ incidentally stored in each of the flooded reservoir phases in the North Ward Estes Field (injection and production rates provided by Whiting Petroleum Corporation; Fig. 3) can be discerned using the following equations:

$$\text{Mole \% of CO}_2 \text{ Retained} = \frac{\text{moles of CO}_2 \text{ Injected} - \text{moles of CO}_2 \text{ Produced}}{\text{moles of CO}_2 \text{ Injected}}$$

$$\text{Rate of CO}_2 \text{ Injected or Produced} = (\text{mol fraction CO}_2)$$

$$\times (\text{Total Gas Rate Injected or Produced})$$

And, the equation suggested by Melzer (2012) to obtain percent of CO₂ stored,

$$\text{CO}_2 \text{ Storage}(\%)$$

$$= \frac{\text{Total CO}_2 \text{ Injected} - \text{CO}_2 \text{ Produced} - \text{CO}_2 \text{ Losses}}{\text{Purchased CO}_2 \text{ Injected}}$$

where CO₂ losses are defined as both surficial losses (typically small volumes that escape the major processing stream or that must be flared/vented during system shut downs), and subsurface losses (typically due to lateral escape from the target sand; Melzer, 2012). Measuring CO₂ losses would require a measurement of anticipated or actual CO₂ losses above the surface, which was unavailable for this study. Therefore, simply mol% of CO₂ retained in each miscible CO₂ flood project will be presented.

The cumulative (over the lifetime of the project) gas injection and production volumes for each project vary between project phases (Table 1). The values presented in Table 1 reflect the cumulative (mixed) gas injection and production volumes across the entire project phase throughout the lifetime of the project as of November 2013. Using these values combined with the average mol% of CO₂ for the injected and produced gas for each project phase (2008, 2010, 2013) and equation 1, the total CO₂ injected into and produced from each project phase could be calculated (Table 1). It is important to reiterate that the injection and production volumes were taken at the end of November 2013, that CO₂ is still being injected into these three project phases, and that daily injection and production rates varied (and continue to vary) throughout the lifetime of each miscible CO₂ flood project considered for this study.

All three miscible CO₂ projects are retaining CO₂ from injection to production (typical of immature EOR projects; Melzer, 2012) at amounts of 39%, 49% and 61% for the 2008, 2010, and 2013 projects, respectively (Fig. 4). These data agree with others, and confirm that both incidental retention of CO₂ occurs in full-scale (i.e., non-pilot sites) miscible CO₂ flood sites (e.g. Melzer, 2012; Hill et al., 2013), and that CO₂ recovery increases over time. Melzer (2012) suggests that, once CO₂ miscible flood projects reach full maturity, the instantaneous retention remains close to 30%, and that initially,

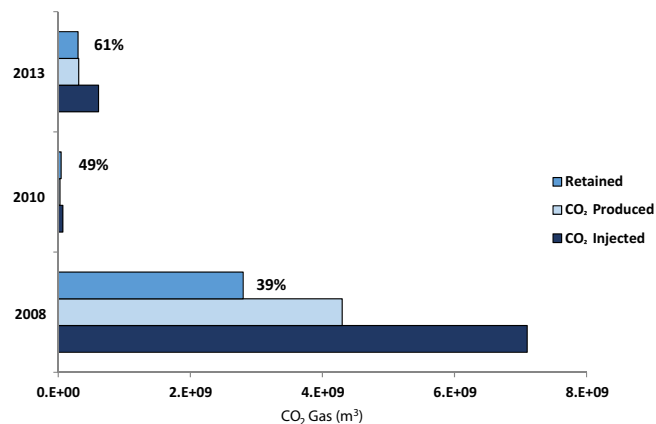


Fig. 4. Cumulative volumes of CO₂ gas both injected and produced from the start of each respective project through November 2013 (written communication, Whiting Petroleum Corporation). Volumes were calculated using total gas production and injection rates multiplied by gas composition data collected for this study. The difference between injected and produced CO₂ rates (i.e., CO₂ retention) are also represented (labeled “Retained”), with each percent retention value to the right of the associated bars.

up to 100% of the injected CO₂ could be retained. Therefore, none of these three projects are likely mature.

5.3. Isotopic evidence for CO₂ trapping during miscible CO₂ flooding

With incidental CO₂ storage occurring in the miscible CO₂ flood projects evaluated for this study, it is important to determine if permanent CO₂ trapping mechanisms are occurring, or if this residual CO₂ is migrating out of the target areas. The major permanent CO₂ trapping and storage mechanisms typically considered for CO₂ sequestration are residual trapping, buoyant trapping, solubility (or dissolution) trapping, and mineralization (e.g., Baines and Worden, 2004; Gilfillan et al., 2009; Brennan et al., 2010; Blondes et al., 2013; Cohen and Rothman, 2015). During miscible CO₂ flooding projects, trapping of CO₂ is typically due to dissolution into fluids that are trapped in inaccessible pore space or to adsorption to rock surfaces (such as shale and clay; Nuttall et al., 2005; Busch et al., 2008; Kang et al., 2010; Gensterblum et al., 2013; Heller and Zoback, 2014), while CO₂ loss outside of the target formation volume is also a possibility (Melzer, 2012). Incidental CO₂ storage in miscible flood reservoirs is different from permanent CO₂ storage; flood projects actively produce formation fluids that include part of the injected CO₂, whereas formation fluid production may not occur in permanent geologic CO₂ storage projects. Therefore, in active miscible CO₂ flooding projects, CO₂ can only be stored (i.e., is not produced) as either a supercritical phase in the subsurface or dissolved in the oil and water that is trapped in areas inaccessible by the circulating fluids, such as dead end pores, or it could be lost by traveling outside of the target reservoir, where it remains in a (possibly) inaccessible part of the formation or adjacent formations.

Historically, δ¹³C–CO₂ has been used independently or in conjunction with noble gas isotopes to track CO₂ fate and transport in sequestration or analogue sites (e.g., Raistrick et al., 2006; Myrntinen et al., 2012a; Gilfillan et al., 2014; Shelton et al., 2014). For this method to be successful, research suggests that the injected gas must be isotopically distinct (i.e., the δ¹³C–CO₂ value of the injected gas must be around 10‰ different than the formation’s pre-injection δ¹³C–CO₂ value) from the original pre-injection formation gas (e.g., Johnson et al., 2009; Mayer et al., 2015). This is the case for the pre-injection conditions for the current study, as the source gas (i.e., McElmo Dome and Doe Canyon gas), and produced gas from the Waterflood project phase have δ¹³C–CO₂

values that are ~10‰ different (Table 2). However, the current $\delta^{13}\text{C}-\text{CO}_2$ values for produced and injected gas for the 2008 and 2013 EOR projects are, on average, within analytical error of source gas $\delta^{13}\text{C}-\text{CO}_2$ values.

This similarity suggests that no active fractionation mechanisms are occurring, particularly, that CO_2 dissolution and mineralization are not occurring, as dissolution of CO_2 into water would cause an isotopic shift in the $\delta^{13}\text{C}-\text{CO}_2$ value of formation gas compared to injected gas (e.g., Mook et al., 1974; Myrntinen et al., 2012b). The lack of fractionation could also be due to short residence times of the injected gas, preventing isotopic equilibrium fractionation effects, or due to the system simply being out of partitioning equilibrium. Unlike $\delta^{13}\text{C}-\text{CO}_2$ values, isotopic equilibrium of noble gas systems is indicated by lack of fractionation of the associated isotopes (i.e., a noble gas system at isotopic equilibrium will not be fractionated) (Prinzhofer, 2013). This is also supported by comparing the $\text{CO}_2/{}^3\text{He}$ values from the injected gas to the produced gas for the 2008 EOR project phase (Table 3). Dissolution (and subsequently, mineralization) would cause a decrease in this ratio compared to a non-dissolved gas; ${}^3\text{He}$ is conservative, and CO_2 concentrations in the gas would decrease as CO_2 dissolves into the formation fluids (e.g., Gilfillan et al., 2008, 2009). The $\text{CO}_2/{}^3\text{He}$ values for the injected gas and the produced gas for the 2008 project phase are similar (all are within analytical error). The $\text{CO}_2/{}^3\text{He}$ values for the 2013 project phase show a bit more variation when comparing the average value for the injected gas to the produced gas – the production wells, on average, produce gas with a lower $\text{CO}_2/{}^3\text{He}$ ratio than the injection wells. This indicates that some CO_2 dissolution is likely occurring.

For this study, there are three major gas endmembers: (1) injection gas (mixture of natural CO_2 , purchased CO_2 , and recycled produced gas (mostly CO_2) from the North Ward Estes Field); (2) pre-injection formation gas representing background conditions; and, (3) produced gas. In the North Ward Estes Field, produced gas is recycled and mixed with newly purchased natural CO_2 ; this mixture is injected into all of the miscible CO_2 flood projects across the field. The pre-injection formation gas geochemistry will be inferred from the gas geochemistry of the Waterflood project, which has never been under an active gas injection. Differences in the noble gas concentrations in the 3 gas endmembers were examined to determine if active fractionation is occurring across the two project phases. In order to assess geochemical deviations from the injected and produced gas in both the 2008 and 2013 projects, any isotopic variation outside of the standard deviation of the injected gas will be considered significant.

When comparing the gas geochemistry for the 2008 and 2013 projects, most of the average values for the measured chemical constituents in the injected and produced gas, when compared to each other, are within analytical error of the measurement (e.g., R/R_A values, ${}^{20}\text{Ne}/{}^{22}\text{Ne}$). The 2013 injected and produced gas is fairly uniform, albeit different $\text{CO}_2/{}^3\text{He}$ ratios. The gas injected during the 2008 EOR project phase was somewhat variable (e.g., ${}^4\text{He}/{}^{20}\text{Ne}$ ratios), while the produced gas sampled across the 2008 project was relatively uniform, with chemical constituents generally within error of each other (e.g., R/R_A values). This creates a problem as the injected gas across each miscible CO_2 flood project in the North Ward Estes Field should be geochemically similar if sampled at the same time – the injection gas geochemistry should not vary beyond analytical error as it is all from the same source. These differences suggest that the injection gas is not uniform, that isotopic fractionation is occurring during transport of the gas to each injection well (e.g. Bouchard et al., 2011), and/or that sampling or analytical errors occurred causing differences in the geochemical composition of the gas (e.g., some sample contamination could have occurred).

The 2013 miscible CO_2 flood project, the more likely of the two projects to be out of geochemical equilibrium (as it is a more recent

flood initiation date and is likely experiencing some CO_2 dissolution) has a fairly uniform injection gas, as shown by many noble gas concentration and ratio standard deviations falling within the error of the analytical measurements. Produced gases from the 2013 EOR project are geochemically distinct (outside analytical error) from the injection gas, with different ${}^4\text{He}$ concentrations and ${}^3\text{He}/\text{CO}_2$ ratios. The difference in $\text{CO}_2/{}^3\text{He}$ is likely due to some dissolution, as discussed previously, while the difference in ${}^4\text{He}$ content between the injected and produced gas is likely due to the injected CO_2 stripping innate helium out of the reservoir (e.g., Györe et al., 2015). Gases injected during the 2008 EOR project are fairly variable when compared to each other (i.e., gases entering different injection wells), while produced gas is geochemically similar to the average composition of the injected gas. Therefore, the 2008 EOR project phase is likely at equilibrium, because no noble gas fractionation is occurring, the residence time of the gas in the system is too short to reflect any isotopic disequilibrium, or that simply, the volume of CO_2 injected over such a short time is so large that there is no longer any storage capacity for it via dissolution.

5.4. Estimating incidental storage of CO_2 in the North Ward Estes field

As the isotopic evidence suggests little active dissolution in the two full scale miscible CO_2 flood project phases in the North Ward Estes Field, other storage mechanisms must be considered. A simple mass-balance approach was used to determine the amount of CO_2 that could be residually stored in dead end (non-swept, inaccessible) pores by calculating the volume of pore space inaccessible by the miscible CO_2 flood efforts. Current volumes of CO_2 dissolved in formation fluids were also estimated using the maximum solubility of CO_2 in inaccessible pore-related reservoir fluids and the volume of those fluids residing in the subsurface.

Volumes of CO_2 unaccounted for by solubility trapping must be either absorbed to mineral surfaces (although this volume is likely minimal due to active pumping of the reservoir fluids), trapped in a pure phase (i.e., as a supercritical fluid) in dead end pores (displacing other fluids) or, the gas traveled outside of the target reservoir. We initially assume that all inaccessible pore space is filled with a mixture of water and oil at different saturations. We then estimate the possibility for residual trapping, assuming that part of this inaccessible pore space is also filled with pure-phase supercritical CO_2 (we assume that buoyant trapping is not occurring due to active production).

5.4.1. Estimating incidental storage in formation water

In order to provide estimates for CO_2 incidentally stored in inaccessible formation water, estimates of inaccessible pore space in each reservoir were required. Before the initiation of the miscible CO_2 flood, both the 2008 and 2013 projects were estimated to be at 68% residual water saturation (written communication, Whiting Petroleum, 2015), while post miscible CO_2 flood operations tend to leave reservoirs at ~80% residual water saturation. Therefore, we assume that at least 20% of the total pore space remains unaffected (i.e., not contacted by injected CO_2 and water) by a miscible CO_2 flood EOR effort, and, of that unswept pore space, on average, 20% is filled with oil. Therefore, we will estimate that unswept pore space will fall between 20 and 40%, and that the fluids in this inaccessible pore space are 80% water and 20% oil.

Using produced water pH, in-situ conditions, and the above mentioned unswept pore space estimates, the CO_2 concentration in produced formation brine could be calculated for both of the 2008 and 2013 flood projects (Tables 4 and 5). It is important to note that the pH of the formation waters (measured at the surface) will change at higher pressures and temperatures (i.e., in-situ conditions), and that some minerals may have salted out (compound

Table 4
Parameters used for CO₂ Dissolution and Storage Calculations CO₂ Dissolution and Storage Volumes.

	2008 EOR	2013 EOR		2008 EOR	2013 EOR
Average pH	7.6	7.3	Total Volume of CO ₂ Gas Indidentally Stored as of November 2013 (m ³ at STP)	2.8 × 10 ⁹	4.3 × 10 ⁷
Approximate Reservoir Temperature (°C)	28	28	Volume of CO ₂ Dissolved in Inaccessible Formation Water at 40% Inaccessible Volume (m ³)	2.9 × 10 ⁷	4.7 × 10 ⁶
Approximate Reservoir Pressure (atm)	82	95			
Average CO ₂ Content (mol fraction)	0.97	0.96	Volume of CO ₂ Dissolved in Inaccessible Formation Oil at 40% Inaccessible Volume (m ³)	1.4 × 10 ⁶	4.7 × 10 ⁵
Approximate PCO ₂ (atm)	80	91	% of Indidentally Stored CO ₂ accounted for with 40% Inaccessible Volume	1.1%	12.0%
Approximate Reservoir Thickness (m)	18	16	Volume of CO ₂ Dissolved in Inaccessible Formation Water at 20% Inaccessible Volume (m ³)	1.5 × 10 ⁷	2.4 × 10 ⁶
Average Porosity (%)	16	16			
Project Surface Area (m ²)	1.5 × 10 ⁷	5.2 × 10 ⁶	Volume of CO ₂ Dissolved in Inaccessible Formation Oil at 20% Inaccessible Volume (m ³)	7.2 × 10 ⁵	2.4 × 10 ⁵
Total Pore Space (m ³)	4.3 × 10 ⁷	1.3 × 10 ⁷	% of Indidentally Stored CO ₂ accounted for with 40% Inaccessible Volume	0.8%	11.2%
Maximum Inaccessible Pore Space (%)	40	40	Supercritical CO ₂ Stored in Maximum (40%) Inaccessible Pore Space (m ³ at STP)	7.0 × 10 ⁹	2.2 × 10 ⁹
Minimum Inaccessible Pore Space (%)	20	20			
K _H	10 ^{-1.503}	10 ^{-1.503}	% of Indidentally Stored CO ₂ accounted for as Supercritical in 40% Inaccessible Volume	250%	5116%
K ₁	10 ^{-6.33}	10 ^{-6.33}	Supercritical CO ₂ Stored in Minimum (1%) Inaccessible Pore Space (m ³ at STP)	1.8 × 10 ⁸	5.6 × 10 ⁷
K ₂	10 ^{-10.31}	10 ^{-10.31}			
[TIC] _{reservoir} (mol/L)	49.4	26.7	% of Indidentally Stored CO ₂ accounted for as Supercritical in 1% Inaccessible Volume	6%	130%

Approximate partial pressure of CO₂ (PCO₂) calculated using formation pressure (supplied by Whiting Petroleum), and average mol% CO₂; equilibrium constants calculated using approximate reservoir temperature and temperature-dependent equations from Clark and Fritz (1997); average reservoir thickness, porosity, temperature, and minimum water saturation supplied by Whiting Petroleum. Inaccessible pore space refers to pore space that is not swept by fluids during the miscible CO₂ flooding operations. Inaccessible formation water and oil refers to the water and oil trapped in inaccessible, non-swept pore space. STP refers to standard temperature and pressure.

speciation changes due to pH) before geochemical measurements; therefore, these calculations are simply an estimate for the current in-situ geochemical conditions.

Using these values and equilibrium partitioning coefficients (temperature dependent equations for K_H, K₁, and K₂ found in Appelo and Postma, 2005) we can estimate the number of moles of CO₂ that can be stored via dissolution trapping. The equilibrium carbonate partitioning equations are as follows:

$$[CO_{2(aq)}] = K_H \times P_{CO_2}$$

$$[H_2CO_3^*] \cong [CO_{2(aq)}]$$

$$K_1 = \frac{[H^+][HCO_3^-]}{[H_2CO_3^*]}$$

$$K_2 = \frac{[H^+][CO_3^{2-}]}{[HCO_3^-]}$$

$$[Total\ Inorganic\ Carbon]_{Reservoir} = [CO_3^{2-}] + [HCO_3^-] + [H_2CO_3^*]$$

After calculating temperature-dependent K values and using the pH to calculate [H⁺] concentration, the total inorganic carbon (TIC) concentration (mol/L) of the produced water can be calculated (Table 4). To determine the amount of CO₂ currently trapped in dead end pores filled with this formation water, the volume of

water possibly retained in each reservoir was calculated using

$$\begin{aligned} & \text{Total Reservoir Pore Space} \times \text{Percent Inaccessible Water Saturation} \\ & \times [TIC] = \text{moles of CO}_2 \text{ retained in formation water} \end{aligned}$$

where the total reservoir pore space was calculated using reservoir thickness, average porosity, and project surface area; and the percent inaccessible water saturation was calculated by multiplying the total inaccessible pore space (40–20% total pore space) by the estimated water saturation (80%) of that inaccessible pore space (Table 4). In order to convert moles of CO₂ to volume of CO₂, van der Waals equation was used, with van der Waals constants (a: 3.592 L²atm/mol²; b: 0.04267 L/mol) for CO₂ applied (Weast, 1969).

Using the above assumptions and equations, the maximum and minimum CO₂ contents dissolved in residual formation water for each project phase were calculated. For the 2008 project, the maximum CO₂ content dissolved in residual formation water is 2.9 × 10⁷ m³, while the minimum CO₂ content is 1.5 × 10⁷ m³ (Table 4). For the 2013 project, the maximum dissolved CO₂ content is 4.7 × 10⁶ m³, while the minimum CO₂ content currently dissolved in residual formation water is 2.4 × 10⁶ m³ (Table 4). The maximum CO₂ content was calculated using an unswept pore space value of 40%, while the minimum CO₂ content dissolved in residual formation water was calculated using an unswept pore space value of 20%. These unswept pore space values were combined with a residual water saturation value of 80% to get estimates for maximum and minimum CO₂ stored via dissolution in residual formation water. The variation in volumes of CO₂ calculated for each miscible CO₂ flood project (2008 versus 2013) stems from differences in project surface area, pH, the partial pressure of CO₂

(which is a function of CO₂ content and average reservoir depth), and reservoir thickness.

5.4.2. Estimating incidental storage in formation oil

Supercritical CO₂ is also very soluble in oil, and forms a mixture if the minimum miscibility pressure is achieved in-situ. The solubility of CO₂ in oil is dependent upon the reservoir temperature, saturation pressure, and the viscosity (API gravity) of the oil (Welker, 1963; Simon and Graue, 1965; Chung et al., 1988). CO₂ dissolution will also cause the crude oil to swell by a factor of 1.32 at 30 °C (Abedini and Torabi, 2014). We used this swelling factor to adjust for the amount of volume accessible by CO₂ saturated oil, meaning, we assume the oil is saturated with CO₂ and that it will swell to 1.32 times its original volume. We assumed, again, that the maximum and minimum percentages of unswept of pore space are 40% and 20%, and that of those percentages, 20% is filled with residual oil (the remaining 80% is filled with residual water). Those estimated pore spaces were then adjusted by the swelling factor, 1.32, to account for changes in volume due to CO₂ mixing with oil.

The volume of CO₂ capable of dissolving in the inaccessible formation oil could be estimated using reservoir parameters (Table 4), the oil-saturated inaccessible pore space, the swelling factor to adjust inaccessible volume (8% at 40% inaccessible pore space and 6.1% at 20% inaccessible pore space), and by using CO₂ solubility information (0.55CO₂ mol fraction for the 2008 project and 0.59 CO₂ mol fraction for the 2013 project) from Mulliken and Sandler (1980). The maximum (8% of total pore space) saturation gives CO₂ saturation values of 1.4×10^6 m³ and 4.7×10^5 m³ CO₂ for the 2008 and 2013 projects, respectively, while the minimum saturation (6.1% swelled oil saturated pore space) produces values of 7.2×10^5 m³ of CO₂ and 2.4×10^5 m³ of CO₂ for the 2008 and 2013 projects, respectively (Table 4). The variation seen between flood projects again stems mostly from differences in project surface area and reservoir thickness.

5.4.3. Estimating incidental storage as supercritical CO₂

It is also possible for supercritical CO₂ to displace unswept fluids and fill portions of the unswept pore space. Volumes of CO₂ that can fill pore space as a supercritical fluid can be estimated assuming 1%–40% of the total pore space is filled with supercritical CO₂, and accounting for compressibility effects of CO₂ gas as it moves to a supercritical state (using 2.3 thousand ft³/reservoir barrel for the 2008 EOR project and 2.4 thousand ft³/reservoir barrel for the 2013 EOR project; Jarrell, 2002). If 40% of the pore space was available for supercritical CO₂ to reside, 7.0×10^9 m³ of gas at surface conditions could be incidentally stored in the 2008 EOR project, while 2.2×10^9 m³ of CO₂ gas (also at STP) could be incidentally stored in the 2013 EOR project. These values, again, represent the volumes of gas that could be stored if measured at standard temperature and pressure, which is why they are larger than the total available pore space in the reservoir (Table 4). If only 1% of the available pore space was filled with supercritical CO₂, the 2008 EOR project could incidentally store 1.8×10^8 m³ of CO₂, while the 2013 project could incidentally store 5.6×10^7 m³ of CO₂ (Table 4).

5.4.4. Other mechanisms of incidental storage

Additional residual CO₂ could be accounted for if active dissolution into either the injected formation water (used for the EOR water-alternating-gas method), and/or the water that is in the “swept” portion of the reservoir, is occurring. Although these fluids (and the associated dissolved CO₂) will eventually be produced, these fluids could serve as an important real-time sink for CO₂ and could account for some of the residual CO₂ at any given point in time. The 2008 EOR project is producing water with alkalinity values similar to the alkalinity value of the water that is being injected across the entire North Ward Estes Field; the average alkalinity for

the 2008 project is 23.5 meq/kg, while the water injected (labeled “Water Injector” in Table 2) across the field has an alkalinity of 24.1 meq/kg (Table 2). This indicates that the producible formation water for the 2008 project is likely saturated in CO₂ and not actively dissolving more injected CO₂. This conclusion is further supported by CO₂/³He ratios, as discussed previously; the value for that ratio does not change across the 2008 project, indicating a lack of active CO₂ dissolution.

The average alkalinity value for waters produced from the 2013 project is lower than the alkalinity value of the injected water, averaging 12.7 meq/kg. This could suggest that the injected water is adding a carbon source to the subsurface and that the formation water in the 2013 project is likely not yet saturated in CO₂, or that there could be losses of inorganic carbon in the system, lowering alkalinity values. However, due to the difference in CO₂/³He values when comparing the injected gas to produced gas for the 2013 project, it appears that CO₂ may still be dissolving into the formation waters. That dissolution could be driven by internal dissolved inorganic carbon (DIC) losses, however, as stated previously. Using the average alkalinity value of the Water-flood project (7.6 meq/kg; Table 2) as an approximation for pre-CO₂ injection reservoir hydrochemistry, the formation water of the 2013 project (average alkalinity 12.7 meq/kg) is approximately 50% less-saturated in carbonate species compared to the 2008 project, but still more saturated than background conditions. Therefore, additional CO₂ (not accounted for in unswept pore space dissolution calculations) could likely dissolve in the formation waters of the 2013 project phase.

5.4.5. Can incidental storage account for residual CO₂?

All of the residual CO₂ for the 2013 EOR project, 4.3×10^7 m³, can be accounted for using a combination of the incidental storage mechanisms mentioned above. CO₂ dissolution into unswept formation water and oil for the 2013 EOR project could account for 5.2×10^6 m³ of CO₂, approximately 12% of the CO₂ currently residing in the subsurface. If simply 1% of the total pore space was filled with pure-phase supercritical CO₂, however, this would account for all of the “lost” CO₂. The 2008 EOR project would require a much larger percentage of the pore space to be filled with supercritical CO₂ to account for the residual CO₂ in the formation. Assuming 40% of the pore space is unswept, and that the fluids within that pore space are saturated with CO₂, this would only account for 3.0×10^7 m³ of CO₂, a little over 1% of the total residual CO₂. In order to account for the residual CO₂, 2.8×10^9 m³, in the 2008 EOR project, 16% of the pore space would have to be filled with supercritical CO₂. Therefore, both the 2008 and the 2013 projects have the storage capacity to justify the residual CO₂ associated with each project.

Both of the reservoirs could potentially be used for permanent geologic CO₂ sequestration post-EOR operations, as no major losses (e.g., CO₂ leakage via faulty wellbores) could be quantified using mass balance. Assuming 80% of each reservoir will be filled with supercritical CO₂, and the remaining 20% will be filled with CO₂ saturated water and oil (at 80% and 20%, respectively), the 2008 EOR project reservoir could store 1.4×10^{10} m³ of CO₂ gas, while the 2013 project could store approximately 4.4×10^9 m³ of CO₂ (at STP). According to the EPA (2014), United States coal fired power plants released, on average 3.81×10^6 metric tons of CO₂ per powerplant in 2010. This equates to 1.94×10^9 m³ of CO₂ (assuming ideal gas behavior and STP). Therefore, the 2008 EOR project could sequester the emissions from one US powerplant for over 7 years, while the 2013 EOR formation could sequester emissions from one US powerplant for over 2 years.

6. Conclusions

This study investigated the fate of injected CO₂ in active EOR projects. McElmo Dome and Doe Canyon natural CO₂ reservoirs were investigated both for CO₂ source and to establish their current gas geochemistry. The source of the McElmo Dome and Doe Canyon produced gas is likely a mix of crustal and mantle-derived gases. Three miscible CO₂ flood project phases and one Waterflood project were examined for formation water and gas geochemistry and isotopic composition. These analyses were used to determine if the retained CO₂ gas in each project phase is incidentally stored in the North Ward Estes Field projects, or if it has been lost to the formation, either on the surface or in the subsurface. Stable isotopes of CO₂ suggested that dissolution of injected CO₂ into formation water was likely not occurring in either the 2008 or 2013 project phases, whereas CO₂/³He values suggest that some CO₂ dissolution is occurring in the 2013 project phase, the younger of the two. Little variation is seen in the noble gas isotopes of the injected and produced gas for the CO₂ flood project phases, indicating the EOR project phases are in isotopic equilibrium and again, that CO₂ dissolution is not an important process currently for these field sites. However, all three CO₂ miscible flood project phases are actively retaining CO₂, at values of 39%, 49% and 61% for the 2008, 2010, and 2013 projects, respectively. Furthermore, the 2008 project could potentially store 1.4×10^{10} m³ of CO₂ gas, while the 2013 project could potentially store 4.4×10^9 m³ of CO₂. Combining these two storage volumes, over 9 years of emissions from an average United States powerplant could be sequestered into these two formations. The current residual CO₂ is likely being stored via previous dissolution into formation water and oil, and via residual trapping in unswept pore spaces.

These results suggest the large capacity of depleted oil reservoirs to residually-trap CO₂ during CO₂ sequestration, which could have global implications for potential geological CO₂ sequestration for combating global climate change. However, additional natural tracer studies focusing on CO₂ leakage in miscible CO₂ flood sites will be necessary before implementing full scale CO₂ sequestration efforts in these (and other) sites.

Acknowledgements

The U.S. Geological Survey's Carbon Sequestration – Geologic Research and Assessments Project provided the majority of the funding for this study. The American Association of Petroleum Geologist's Grants-in-Aid Program, the Poate Graduate Fellowship, the Sussman Foundation, and the Geological Society of America also supported this research. We thank both Kinder Morgan LLC (especially C. Bryant, L. Hill, and D. McMurrey) and Whiting Petroleum (especially, D. Entzminger) for allowing access to field sites and for their helpfulness and cooperation throughout the investigation, as well as R. Olea and two anonymous reviewers for providing helpful insight to the manuscript. Any use of trade, firm, or product names is for descriptive purposes only and does not imply endorsement by the U.S. Government.

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