



Assessing geochemical reactions during CO₂ injection into an oil-bearing reef in the Northern Michigan basin

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ABSTRACT

The Dover 33 Reef, part of the Niagaran Reef Complex in Northern Michigan (USA), has been the focus of an enhanced oil recovery/carbon capture utilization and storage (EOR/CCUS) project as part of the Phase III-Midwest Regional Carbon Sequestration Partnership (Gupta et al., 2013a,b). The Dover 33 structure has experienced significant CO₂ flooding in the past two decades, and over the course of the current injection study (between February 2013 and July 2016) has received approximately 100 to 1000 tonnes/day into the central injection well (L-M) 1–33). As part of the geochemical monitoring effort of the study, gas and fluid samples were collected from Dover 33 reef, and several other nearby reef structures, to assess the impact of CO₂ injection on the geochemical processes occurring within in the reef.

The injected gas is composed of approximately 95% CO₂, with a $\delta^{13}\text{C}_{\text{CO}_2}$ of $\sim 20.5\text{‰}$, which is consistent with previously published compositions of Antrim shale gas, the source of the CO₂. The concentrations and isotopic compositions of higher pressure gas collected from the L-M 5–33 monitoring well were similar to those measured in the injection well, but did exhibit a small but systematic shift in isotopic composition towards lower values over the course of the study, suggesting mixing and dilution between the gas in the reservoir and the injected gas. In contrast the $\delta^{13}\text{C}_{\text{CO}_2}$ of gas samples from the monitoring well with the lower surface pressure, L-M 2–33, are consistently lower throughout the study, $\sim 18.5\text{‰}$, indicating that reactions with the injected CO₂ are occurring within the reef or with the well casing.

Fluid samples were collected to assess the extent of interaction among the injected gas, the reservoir rock, and the brine. The brine samples are acidic (pH ~ 4.1 to 4.9) with a total salt content of nearly 400 g/L. Analysis of the isotopic composition of dissolved inorganic carbon (DIC) in the Dover 33 brine shows that $\delta^{13}\text{C}$ is higher than the injected gas (27–33‰) suggesting that the gas is not in equilibrium with DIC in the brine, and that there has been little isotopic exchange with carbonate minerals in the reef. The water isotope composition of the brine, $\delta^{18}\text{O}$ and δD , plot below the meteoric water line, indicating that the water is not of recent meteoric origin and has undergone isotopic exchange with both gas and minerals within the reef structure. The $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of the brine samples range from 0.70865 to 0.70869, consistent with Silurian seawater composition.

Geochemical modelling of the brine composition shows that the predicted CO₂ solubility as DIC is much greater than the measured DIC, and that the brines are supersaturated with respect to carbonate minerals, suggesting the potential for significant trapping of CO₂ in both dissolved and mineral form.

1. Introduction

Carbon capture utilization and storage (CCUS) has been used as a strategy to capture CO₂ released from the combustion of fossil fuels and store it in underground repositories in an effort to reduce rising

atmospheric CO₂ concentrations and mitigate global warming or utilize it to increase oil production from reservoirs. The most significant underground storage sites are deep saline aquifers and depleted hydrocarbon (oil and gas) fields (e.g., Benson and Cole, 2008; Boreham et al., 2011; DePaolo and Cole, 2013; Jenkins et al., 2012; Kharaka et al.,

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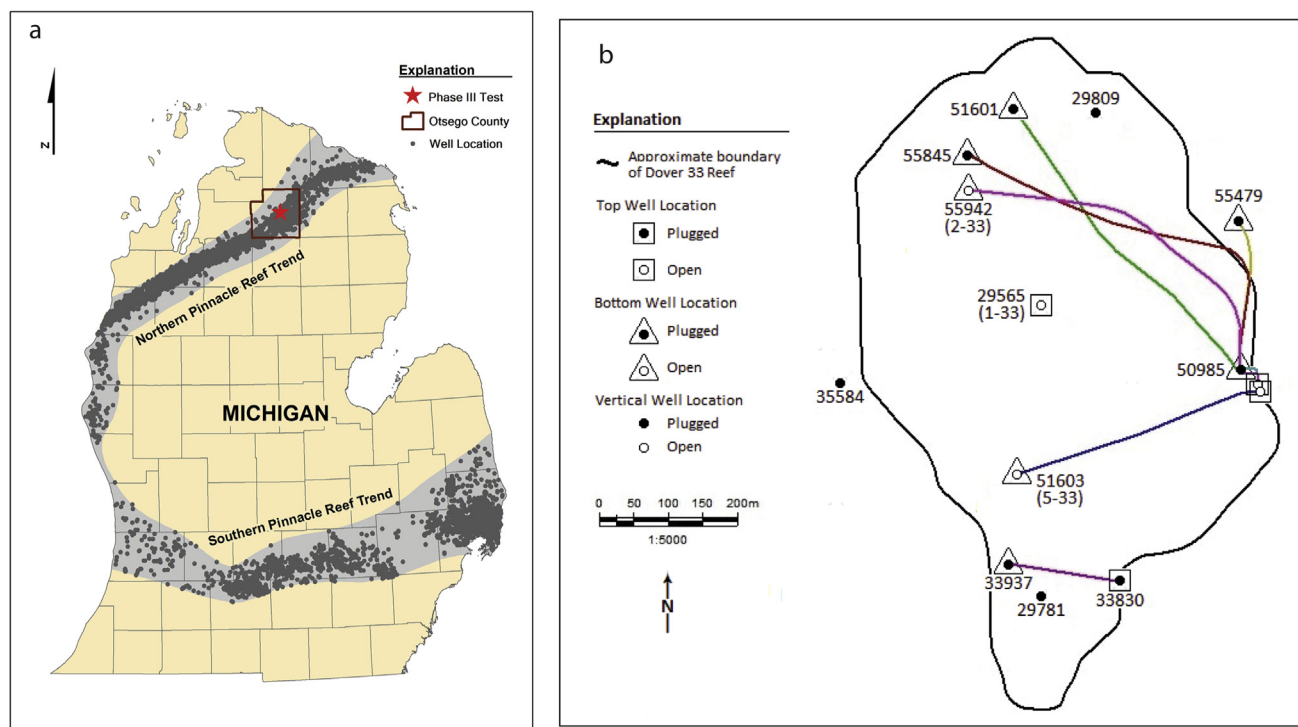


Fig. 1. (a) Site location of the Dover 33 reef (position of red star) in Otsego County, northern Michigan (USA); (b) Reservoir plan view with well layout. Injection well is the L-M 1–33, monitoring well 1 is the L-M 2–33, and monitoring well 2 is the L-M 5–33. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

2006, 2013; Lu et al., 2012; Mayer et al., 2013) which have the added advantage of utilizing the injected CO₂ in enhanced oil recovery (EOR). Natural isotopic tracers are widely used in CCUS studies (Johnson et al., 2011a,b; Kharaka et al., 2013; Li and Pang, 2015; Mayer et al., 2013) in order to determine geochemical processes occurring in the deep subsurface, the rates of CO₂ interaction with subsurface brine, oil, and rocks, and the fate of the injected gas.

Multiple processes can affect the fate and transport of CO₂ in the subsurface including hydrodynamic processes such as advection, dispersion, and mixing/dilution, as well as chemical processes such as diffusion into low permeability materials, partitioning into non-aqueous phases (e.g., oil), dissolution/precipitation of carbonate minerals, and water/rock interactions (Hitchon, 1996). Identifying and quantifying the processes affecting CO₂ transport for a given subsurface environment is essential for predicting the residence time of CO₂ and estimating the storage characteristics and capacity of that reservoir. Whereas reservoir models can be designed to simulate those processes, the accuracy of these models depends upon input parameters that adequately represent *in situ* conditions and on careful validation through field testing.

Geochemical tracers utilizing gas, brine, and isotope compositions have become an important tool for *in-situ* subsurface characterization, allowing detailed interrogation of complex systems with moving, mixing, and reacting components. For example, naturally-occurring stable isotopes of the light elements (O, H, C, S, N) have been used extensively to determine the sources of fluid and gas species and their mechanisms of migration, to assess the extent of fluid/rock interactions, and to quantify the residence times of fluids in the subsurface (e.g., Boreham et al., 2011; Emberley et al., 2004; Mayer et al., 2013, 2015). Naturally occurring constituents and their isotopic compositions have a number of benefits for geochemical applications: (a) they commonly occur in a variety of earth materials – gas, brine, and rock; (b) sensitive mass spectrometric methods exist for quantifying their abundance and/or isotopic ratio; and (c) many of the necessary kinetic and equilibrium partitioning data are available to interpret these processes.

The proposed injection of large-volumes of CO₂ into different types of geological formations (e.g., aqueous, coal-bed, oil and gas fields) provides an opportunity for the use of isotope monitoring techniques. This is because the injected CO₂ can be treated as an applied tracer derived from anthropogenic or other sources, which should have a very distinct isotopic signature compared to that of background atmospheric CO₂, soil/groundwater CO₂ or the *in situ* CO₂. Stable isotopes have been used extensively and successfully as indicators in the hydrogeology, oil/natural gas exploration, and geothermal resource assessment (e.g., Cantucci et al., 2009; Kharaka et al., 2013; Kharaka and Cole, 2011; Kendall and McDonald, 1998; Tissot and Welte, 1984). By accounting for how stable isotopes of carbon and oxygen in CO₂ ($\delta^{13}\text{C}$ and $\delta^{18}\text{O}$) vary during the injection process, we can (a) understand complex natural geochemical processes involving CO₂ in the subsurface, and (b) assess and monitor quantitatively both short- and long-term consequences of subsurface CO₂ injection and sequestration, and possible leakage from system. A complex set of physical and chemical reactions occurring among the gaseous, solution, and solid phases in the subsurface should be anticipated which, in turn, will lead to a variety of isotopic fractionation trends.

A number of processes can influence the chemical and isotopic signals in gas, fluids and solids, including mixing between fluid or gas in the reservoir, dissolution or exsolution of gases between brines and hydrocarbons, sorption onto mineral surfaces, microbially mediated reactions, fluid-rock interactions and mineralization. Changes may occur in the overall geochemistry or the isotopic signatures of the fluids or gas in the reservoir as a result of these geochemical mechanisms. The purpose of the geochemical monitoring is to use stable and radiogenic isotope geochemistry in concert with analysis of general geochemical parameters of fluids and gases to determine geochemical processes occurring in the reef structure as a result of CO₂ injection.

1.1. Study site

The primary field site for the geochemical study is the Dover 33

reef, part of the Silurian Niagaran northern reef complex near Gaylord, Michigan, USA (Fig. 1) (Barnes et al., 2013; Gerst et al., 2014; Gupta et al., 2013a,b; Kelley et al., 2014; Ravi Ganesh et al., 2014). This reef is typical of Silurian Niagaran pinnacle reefs that form a southern and a northern trend—both curvilinear—and situated in the Michigan Basin. The Dover 33 reef is part of the northern trend, one of more than 700 pinnacle reef structures that follow a SW-NE trending band approximately 250 km long (Charpentier, 1989; Ravi Ganesh et al., 2014; Toelle et al., 2008). These carbonate reef structures are approximately 100–200 m (300–600 feet) high, although they currently are buried to depths of approximately 1000–2200 m below surface (Charpentier, 1989). A recent geological model for Silurian pinnacle reef structures suggests that they are asymmetrical in shape, with a sedimentary rock apron situated along the flanks of a carbonate reef core whose slope and lateral extent depend on paleowind direction (Rine et al., 2016). Much of the reef carbonate facies have been dolomitized, although more extensively so in the southern trend. Within the northern trend, there is less dolomitization, with more calcite comprising reefs located closer to the basin (Sears and Lucia, 1979; Rine et al., 2016). Approximately 400 million barrels of oil—an estimated 25 percent of oil in place in the northern reef trend—were produced from these structures over four decades of production indicating significant potential oil reserves that could be extracted by enhanced oil recovery (EOR) (Toelle et al., 2008).

Injection of CO₂ into the Dover 33 reef, along with geophysical monitoring and modelling, has been integral to EOR/CCUS research as part of the Phase III Midwest Regional Carbon Sequestration Partnership (MRCSP) (www.mrcsp.org) (Barnes et al., 2013; Gerst et al., 2014; Gupta et al., 2013a,b; Kelley et al., 2014; Ravi Ganesh et al., 2014). The Dover 33 reef structure has seen significant CO₂ flooding in the past two decades for EOR, and details of prior injection and production are presented in Kelley et al. (2014). From January 1996, through December 2008, approximately 1.29 million tonnes of CO₂ were injected into the reef, and prior to the current injection study, approximately 200,000 tonnes of this CO₂ were retained in the reef (Gerst et al., 2014; Kelley et al., 2014). From January 2008 through December 2012 there was much lower activity in this reef as compared to the previous 12 year interval. The CO₂ used for the current injection study, and for more recent CO₂ flooding (prior to the Phase III injection study) is sourced from the stratigraphically shallower Antrim Shale (Toelle et al., 2008). This gas was not analyzed for its isotopic composition prior to the injection tests, though there have been several studies that have focused on the composition of gas from the Antrim Shale (Martini et al., 1996, 2003, 2008). The CO₂ that was injected for the EOR was recycled through several nearby reef structures to a central processing facility (Dover 36 CPF) to recover the oil and reuse the gas. During the Phase III injection study (started in early 2013) CO₂ was not removed from the Dover 33 reef.

In the current phase of the project, approximately 100 to 1000 tonnes/day were injected into the central injection well (L-M 1–33) during periods of active injection to investigate CCUS and reef integrity in these pinnacle reefs (Kelley et al., 2014). Approximately 244,000 tonnes of CO₂ were injected from February 2013 through August 2014 (Gerst et al., 2014). However the injection rate was not constant, and instead consisted of several periods of injection (lasting from hours to weeks) followed by downhole pressure monitoring to determine how the reef would respond to CO₂ injection. The ‘baseline’ sampling for the geochemical monitoring aspects of the study was done in the weeks prior to the first injection test, and then sampling for geochemical monitoring was done during the pressure/injection tests as opportunities arose. Although CO₂ was injected as a supercritical fluid, pressure and temperature measurements in the reef structure (made using downhole pressure/temperature gauges) suggest that phase changes occurred over time, from vapor to liquid and then back to a supercritical fluid as pressure increased (Kelley et al., 2014). All of these past and current engineered activities make monitoring and interpreting the fate of CO₂ and its interaction with the brine very challenging.

1.2. Wells

The Dover 33 reef structure covers approximately 0.4 km² and has a height of approximately 80 m. The depth to the top of the reef is approximately 1650 m. There are three wells within the reef structure that had not been plugged or abandoned that were used to collect fluid and gas samples throughout the course of this study (Fig. 1). Due to the different casing and directional configurations and changing physical conditions (fluid/gas levels and pressures) in these wells, the sampling techniques and the ability to collect samples were different throughout the study.

The injection well (L-M 1–33) is a vertical well located near the center of the reef (Fig. 1). The total depth of this well is 1726 m, which extends into the Gray Niagaran Formation. Prior to the start of the Phase III injection study, fluid filled the well, allowing for the collection of brine and oil samples. However, after CO₂ injection started (February 2013), the fluid was displaced by the CO₂, and only gas (primarily CO₂) samples could be collected from this well.

The L-M 2–33 monitoring well has a total length of 2174 m measured depth. The surface completion of this well is along the eastern edge of the reef, but a horizontal uncased (lateral) extends to the north and west of the well and continues across the northern portion of the reef. The uncased lateral section acts as a perforated zone over the entire length and is used to monitor the reef at a depth of approximately 1676 m true vertical depth. Based on field observations and analysis of samples collected from the L-M 2–33 well, it appears that the lateral portion of the well, or at least the end of the tubing, is completed within the water saturated zone of the reef. Gas samples could be collected from the wellhead, but the pressure of the samples was near atmospheric and the gas composition was significantly different than for the gas collected from the L-M 1–33 injection well or the L-M 5–33 monitoring well. Fluid samples could only be collected via swabbing the well, and therefore, were collected under minimal pressure. Toward the end of the geochemical study, the tubing filled with formation brine all the way to the surface (suggesting the end of tubing was below the water level in the reservoir).

The L-M 5–33 monitoring well is a deviated well that is used for geochemical monitoring purposes. Initially, the L-M 5–33 well was equipped with a pump jack that could be employed to produce gas and brine samples under pressures similar to reservoir conditions. However, within six months of CO₂ injection, the reservoir pressures had increased to a level such that only gas (primarily CO₂) was being pushed to the wellhead. Subsequently, only gas samples could be collected from the well.

In addition to the primary study site, two brine samples and three gas samples were collected from nearby reefs as proxies for the baseline fluid and gas composition for typical reef structure in this area. Brine samples were collected from the Fieldstone 2–33 well which is located in a lobe of the Dover 33 reef that is semi-isolated (hydraulically) from the main reef. This structure and well experienced increased pressure during the injection tests conducted during the MRCSP Phase III experiments but was not believed to be in contact with the injected gas. Gas samples were also collected from the Charlton 19 reef, also known as El Mac Hills (EMH), wells 1–18, 2–18 and 1–19D. These are monitoring wells in nearby reef structures that were drilled for oil and gas but had not experienced CO₂ flooding at the time of sampling.

2. Methods

2.1. Gas sample collection

A total of 14 gas samples were collected from the three wells during the geochemical study of the Dover 33 reef: three samples from the L-M 1–33 injection well; five samples from the L-M 2–33 monitoring well; and six samples (not including duplicates) from the L-M 5–33 monitoring well. In addition, five gas samples were collected from the Dover

36 Central Processing Facility (CPF) from the pure, recycled and commingled (mixture of pure and recycled gas) gas streams. These represent 'pure' CO₂ recovered from the Antrim Shale, gas to be injected into the reefs, and gas that has passed through the reefs and subsequently removed. Prior to the start of the injection tests, gas was injected and then recycled through several nearby reef structures in addition to the Dover 33 as part of the ongoing EOR in this field. After the injection study commenced, there was no gas recycled from the Dover 33. An additional three gas samples were collected from another nearby reef structure, the Charlton 19 (El Mac Hill (EMH) wells 1–18, 2–18 and 1–19D) in order to estimate 'baseline conditions' for a pinnacle reef that had not experienced CO₂ flooding.

Gas samples from the Dover 33 site and CPF were collected in Swagelok 300 ml stainless steel cylinders (DOT rated 1800 psi) with valves on both ends. Gas samples for the Charlton 19 wells were collected using 300-ml stainless steel containers provided by Isotech Laboratory. These containers also had valves on both ends. All gas sample cylinders had been evacuated in the laboratory prior to sampling. Most of the cylinders were purged for several minutes with the sample gas in the field, however, several of the samples from the L-M 2–33 well were at low (~atmospheric pressure) and were collected by allowing the gas to flow into the evacuated cylinder at the well head.

2.2. Water sample collection

Water samples from the L-M 1–33 and L-M 2–33, and the Fieldstone 2–33 wells were collected by the swab method. Wells were swabbed approximately 10–20 times (to sufficiently purge stagnant water in the wellbore) before fluid samples were collected for chemical analysis. Fluid samples from the L-M 5–33 well were collected from the pump jack. Although fluid was under pressure in the well head, the sample was collected in a large open container at atmospheric pressure, therefore the brine samples likely degassed to some degree. Bulk water samples were allowed to sit for several hours, allowing the brine-oil emulsion to break down, and then the fluid sample was filtered under positive pressure using a 0.45 µm capsule filter into several bottles for various analytical methods. Samples for cation analysis were acidified with trace metal grade nitric acid.

2.3. Analytical methods

Samples were analyzed for major and trace element composition of the brine, isotopic composition of water, ⁸⁷Sr/⁸⁶Sr ratios of dissolved Sr, isotopic composition of dissolved inorganic carbon (DIC), and chemical and isotopic composition of gas.

Analysis of concentrations and isotope composition of major constituents in gas samples were conducted by Isotech Laboratory. Concentrations of major constituents in the gas samples were measured by gas chromatography (GC). The δ¹³C of CO₂ and CH₄, δ¹⁸O of CO₂, and δD of CH₄ were measured by isotope ratio mass spectrometry. The isotopic compositions of C and O for gas species are reported with respect to VPDB, H is reported relative to VSMOW. Typical precision for isotopic analysis is approximately 0.06‰ for δ¹³C of CO₂ and CH₄, and 0.08‰ for δ¹⁸O of CO₂. Analysis of the three higher pressure gas samples collected within several minutes of each other from the L-M 5–33 well had precision of 0.06‰ for δ¹³C of CO₂, 0.06‰ for δ¹⁸O of CO₂, 0.03‰ for δ¹³C of CH₄ and 1.0‰ for δD of CH₄.

Water isotope compositions were measured at Isotech Laboratory or at The Ohio State University using Picarro water isotope analyzers. The instrument at OSU uses a salt mesh to retain salts in the injection port of the vaporizer and an increased injection volume to account for the lower water content in these saline brines. The isotopic compositions of H and O for water are reported relative to VSMOW. Typical precision for isotopic analysis for δ¹⁸O and δD on water using the Picarro instrument at the OSU are 0.5‰ and 2‰ respectively.

The isotopic composition of dissolved inorganic carbon was

measured at the Subsurface Energy Materials Characterization and Analysis Laboratory (SEMCAL), at OSU using either an OI Analytical carbon analyzer, or an Automate Autoprep sampler interfaced to a Picarro Carbon isotope analyzer. Typical reproducibility for replicate analysis of δ¹³C of DIC using the Picarro Carbon isotope analyzer was ~1‰. Analyses were also done using a Thermo Scientific Gas Bench II interfaced to a Delta V mass spectrometer at SEMCAL for comparison to the results obtained from the Picarro. DIC analyses were initially done on fluid samples. However, because the isotopic composition of the DIC can change as the sample degasses, brines collected in October 2013 and those from the Fieldstone 2–33 well were preserved by co-precipitation with ammonia/SrCl₂ (Singleton et al., 2012). Because the isotopic composition of DIC in fluid samples could change over time, only data from samples analyzed soon after collection were used for this study.

Major ions for brines collected from the Dover 33 wells were measured at a commercial laboratory using inductively coupled plasma optical emission spectrometry (ICP-OES) or inductively coupled plasma mass spectrometry (ICP-MS) for cations, ion chromatography (IC) for anions, DIC/DOC using a carbon analyzer and alkalinity by titration. Major ions for the brine collected from the Fieldstone 2–33 well were measured at OSU. Cations and selected trace elements were analyzed using a Perkin Elmer Optima 4300 DV ICP-OES. Samples were diluted by 100–5000 fold in 2% trace metal grade HNO₃ for analysis. Anion samples were diluted by 100–2000 fold with Milli Q™ water and then analyzed using a Dionex ICS-2100 Ion Chromatograph. Typical reproducibility for replicate samples for major element analysis at OSU was within 10%.

Details of analytical methods, accuracy, and precision of Sr isotope analysis are described in Saltzman et al. (2014) and Edwards et al. (2015). All samples were spiked with an ⁸⁴Sr tracer and purified using H⁺ cation exchange resin via two elutions of 2N HCl through silica glass columns (cf. Foland and Allen, 1991). Strontium isotopic compositions were measured using dynamic multicollection on a Finnigan MAT-261A thermal ionization mass spectrometer at the Radiogenic Isotope Laboratory at OSU. Saltzman et al. (2014) report typical precision of 0.000009 (2σ s.d.) for intrarun analysis of samples, and a value of 0.710224 ± 0.000030 for 67 analyses of the strontium carbonate standard SRM 987.

3. Results and discussion

3.1. Gas chemistry and isotopes

Gas samples from the study site were collected in November 2012, May 2013, July 2013, August 2013, October 2013, and December 2013 (Table 1). Originally sampling was planned to be undertaken as a time series to investigate the changes in isotopic composition of the gas and fluids in the reef complex associated with CO₂ injection. However, after the initial samples were analyzed, gas samples were only obtained in conjunction with other activities at the field site. Additional gas samples were obtained after the study period from nearby reef structures (Fieldstone and El Mac Hills) that had never experienced CO₂ flooding in order to estimate the baseline gas composition for the Dover 33 reef.

3.1.1. Dover 36 central processing facility (CPF)

The gas samples collected at the Dover 36 facility had similar concentrations and isotopic compositions during the entire 13-month sampling period. Differences that are observed reflect the source of the gas and mixing of gas within the facility. The compositions of the two high-purity CO₂ gas samples collected in November 2012 and May 2013 are nearly identical (Table 1). The high purity gas is comprised almost entirely of CO₂ (> 99.7%) with mean δ¹³C_{CO2} of 20.37‰ and δ¹⁸O of 2.06‰. This δ¹³C value is consistent with previously published data for δ¹³C_{CO2} of Antrim Shale gas (Martini et al., 1996, 2003, 2008), which is the source of the gas used in this long-term injection study (Gupta et al.,

Table 1

Gas Composition. ($\delta^{18}\text{O}$ in last column is with respect to VSMOW for comparison to the isotopic composition of water).

Sample	Sample	He	H ₂	Ar	O ₂	CO ₂	N ₂	CO	C ₁	C ₂	C ₂ H ₄	C ₃
Name	Date	%	%	%	%	%	%	%	%	%	%	%
Dover 36												
Pure CO ₂ - 8	11/14/2012	nd	nd	nd	0.017	99.74	0.050	nd	0.150	0.0130	nd	0.0107
Pure CO ₂ - 15	5/6/2013	nd	nd	nd	nd	99.73	0.016	nd	0.205	0.0166	nd	0.0128
Comingled CO ₂ - 7	11/14/2012	nd	0.0017	nd	0.009	96.27	0.12	nd	2.31	0.563	nd	0.378
Comingled CO ₂ - 16	5/6/2013	nd	nd	nd	nd	96.12	0.061	nd	2.43	0.621	nd	0.418
Recycled - 17	5/6/2013	nd	nd	nd	nd	94.23	0.10	nd	3.74	0.940	nd	0.580
L-M 1–33												
1-33 - 14	5/6/2013	nd	nd	nd	nd	96.75	0.071	nd	2.30	0.458	nd	0.257
1-33 - 21	7/30/2013	nd	0.0439	nd	nd	95.72	0.055	nd	2.78	0.569	nd	0.300
1-33 - 41	10/3/2013	nd	nd	nd	nd	96.20	0.052	nd	2.43	0.622	nd	0.392
L-M 5–33												
5-33 - 1	11/14/2012	nd	0.0027	nd	0.011	93.94	0.061	nd	2.76	1.44	nd	1.02
5-33 - 2	11/14/2012	nd	0.0023	nd	0.007	94.07	0.061	nd	2.78	1.42	nd	0.960
5-33 - 3	11/14/2012	nd	0.0025	nd	0.010	94.11	0.068	nd	2.81	1.40	nd	0.927
5-33 - 11	5/6/2013	nd	0.502	1.14	2.47	0.036	95.21	nd	0.168	0.0949	0.0002	0.0934
5-33 - 12	5/6/2013	nd	0.477	1.14	2.70	0.045	95.01	nd	0.149	0.0843	0.0002	0.0825
5-33 - 23	7/30/2013	nd	2.59	1.04	5.32	0.17	89.58	nd	0.437	0.153	0.0005	0.165
5-33 - 31	8/20/2013	nd	nd	nd	nd	95.58	0.028	nd	1.10	0.663	nd	0.948
5-33 - 43	10/3/2013	nd	0.437	nd	nd	96.08	0.030	nd	1.33	0.623	nd	0.685
5-33 - 52	12/18/2013	nd	0.0102	nd	nd	96.29	0.041	nd	2.34	0.703	nd	0.412
L-M 2–33												
2-33 - 13	5/6/2013	nd	5.42	0.0981	2.20	79.51	8.45	nd	1.86	0.709	0.0007	0.669
2-33 - 32	8/21/2013	nd	nd	0.901	20.34	0.64	78.09	nd	0.0010	0.0006	nd	0.0019
2-33 - 22	7/30/2013	nd	25.59	0.237	5.36	47.55	20.31	nd	0.191	0.0803	0.0010	0.106
2-33 - 42	10/3/2013	nd	1.26	nd	nd	98.52	0.049	nd	0.0816	0.0119	0.0001	0.0034
2-33 - 51	12/13/2013	nd	nd	0.937	21.05	0.067	77.94	nd	0.0004	nd	nd	nd
El Mac Hills												
EMH 1 - 18	1/27/2015	nd	0.0154	nd	0.017	0.025	0.014	nd	9.5	40.12	nd	34.45
EMH 2 -18	12/31/2015	0.0077	1.48	nd	nd	nd	0.72	nd	67.61	17.63	0.0003	7.95
EMH 1-19D	2/20/2015	nd	0.0212	0.0243	0.6	0.073	2.54	nd	35.82	26.36	nd	20.72
Sample	C ₃ H ₆	iC ₄	nC ₄	iC ₅	nC ₅	C ₆ +	$\delta^{13}\text{C}_{\text{CO}_2}$	$\delta^{18}\text{O}_{\text{CO}_2}$	δDC_1	$\delta^{18}\text{O}_{\text{CO}_2}$	$\delta^{18}\text{O}_{\text{CO}_2}$	$\delta^{18}\text{O}_{\text{CO}_2}$
Name	%	%	%	%	%	%	‰	‰	‰	‰	‰	‰
Dover 36												
Pure CO ₂ - 8	nd	0.0032	0.0052	0.0034	0.0023	0.0053	20.48			1.96		32.88
Pure CO ₂ - 15	nd	0.0035	0.0057	0.0035	0.0025	0.0044	20.25			2.16		33.09
Comingled CO ₂ - 7	nd	0.0856	0.128	0.0564	0.0365	0.0428	20.56	−51.62	−269	2.02		32.94
Comingled CO ₂ - 16	nd	0.0917	0.133	0.0532	0.0340	0.0363	20.51	−51.92	−274	2.51		33.45
Recycled - 17	nd	0.119	0.170	0.0608	0.0366	0.0285	20.49	−52.01	−276	2.40		33.33
L-M 1–33												
1-33 - 14	nd	0.0484	0.0660	0.0228	0.0138	0.0101	20.55	−52.08	−273	2.16		33.09
1-33 - 21	nd	0.0895	0.145	0.0951	0.0660	0.141	20.34	−52.10	−276	1.56		32.47
1-33 - 41	nd	0.0836	0.119	0.0463	0.0286	0.0228	20.48	−51.67	−278	2.5		33.40
L-M 5–33												
5-33 - 1	nd	0.211	0.282	0.115	0.0706	0.0915	20.83	−50.71	−266	4.95		35.96
5-33 - 2	nd	0.192	0.254	0.102	0.0630	0.0856	20.88	−50.71	−268	4.93		35.94
5-33 - 3	nd	0.184	0.244	0.0989	0.0611	0.0814	20.76	−50.65	−266	5.04		36.06
5-33 - 11	0.0003	0.0373	0.0586	0.0457	0.0309	0.116						
5-33 - 12	0.0003	0.0359	0.0531	0.0477	0.0318	0.145						
5-33 - 23	0.0007	0.0665	0.107	0.0836	0.0595	0.225						
5-33 - 31	nd	0.349	0.567	0.313	0.203	0.249	20.20	−50.03	−271	4.20		35.19
5-33 - 43	nd	0.205	0.312	0.138	0.0814	0.0833	20.38	−51.53	−277	10.0		41.16
5-33 - 52	nd	0.0653	0.0865	0.0228	0.0135	0.0129	20.59	−51.84	−261	3.82		34.80
L-M 2–33												
2-33 - 13	0.0003	0.179	0.292	0.148	0.103	0.361	18.73	−48.21	−266	8.87		40.00
2-33 - 32	nd	0.0012	0.0028	0.0031	0.0025	0.0112	18.61			14.02		45.31
2-33 - 22	0.0004	0.0435	0.0870	0.0775	0.0636	0.304	18.12			7.61		38.70
2-33 - 42	nd	0.0005	0.0012	0.0013	0.0013	0.0697	18.75			11.97		43.20
2-33 - 51	nd	nd	nd	nd	nd	0.0011						
El Mac Hills												
EMH 1 - 18	0.0003	5.82	7	1.61	0.822	0.484	na	−50.57	−286			
EMH 2 -18	0.0001	1.37	1.84	0.613	0.369	0.412	na	−50.19	−274			
EMH 1-19D	nd	5.17	5.59	1.77	0.841	0.471	na	−50.13	−268			

2013a,b; Toelle et al., 2008) and should be distinctively higher than the $\delta^{13}\text{C}$ for carbonate minerals in the reef structure or for DIC in equilibrium with these minerals. The high-purity CO₂ gas contains trace amounts of other gases, predominately N₂ and methane, although quantities of these gases were insufficient to determine their isotopic

composition.

The recycled stream represents gas produced (along with oil) from several of the other reef structures before it is combined with other gas streams prior to reinjection into the reefs. The one sample collected from this stream was predominately CO₂, ~94%, with an isotopic

composition that is similar to the comingled or high purity gas stream, $\delta^{13}\text{C}_{\text{CO}_2}$ of 20.49‰ and $\delta^{18}\text{O}$ of 2.40‰. The recycled stream also contains higher concentrations of hydrocarbons ($\text{C}_1\text{--C}_5$), though predominately methane (~3.74%), reflecting the source of this gas.

The co-mingled stream represents a mixture of gas from the recycled stream and the pure CO_2 stream; the two co-mingled samples collected are composed of approximately 96% CO_2 with a mean $\delta^{13}\text{C}_{\text{CO}_2}$ of 20.54‰ and $\delta^{18}\text{O}$ of 2.27‰ (Table 1). The gas from the co-mingled stream travels approximately three miles through a pipeline from the Dover 36 CPF to the L-M 1–33 injection well. Pressure at the injection well was typically ~650 to 700 psi when samples were collected, or about half the pressure of the Dover 36 CPF. The concentrations and isotopic compositions of CO_2 samples collected at the L-M 1–33 injection well are similar to those measured at the gas processing facility, approximately 96% CO_2 with mean $\delta^{13}\text{C}_{\text{CO}_2}$ of 20.46‰ and $\delta^{18}\text{O}$ of 2.06‰ for the three samples collected.

Methane was the predominate hydrocarbon gas measured in samples collected at the Dover 36 CPF, with concentrations ranging from ~0.2% in the pure CO_2 stream to ~2–4% in the recycled and comingled streams. There was insufficient methane in the pure CO_2 stream for an isotopic analysis, however there was little variation observed in the isotopic composition ($\delta^{13}\text{C}_{\text{CH}_4}$ and δD) of methane for the comingled, recycled and injected streams with means of $\delta^{13}\text{C}_{\text{CH}_4}$ and δD of –51.8‰ and –273‰, –52.0‰ and –276‰, and –52.0‰ and –276‰, respectively.

3.1.2. Monitoring wells

There was considerable variability in the compositions and concentrations of gas samples collected from the L-M 5–33 and L-M 2–33 monitoring wells (Table 1). However, these differences are largely due to difficulties sampling at the well head, or atmospheric contamination, either when the sample was collected or when the well head configuration was changed. The low pressure (~atmospheric) samples taken from the L-M 5–33 monitoring well in May and July of 2013 are composed primarily of N_2 , with lesser amounts of O_2 , Ar, H_2 , CO_2 and traces of other hydrocarbons ($\text{C}_1\text{--C}_5$), and thus are not representative of the gas stored within the reef structure. Although N_2 concentrations are greater than N_2 in the atmosphere, Ar/ N_2 ratios are similar to atmospheric composition, ~0.012. In addition, these gas samples contained coexisting H_2 and O_2 , reflecting a mixing of gas that reacted with the corroded steel pipe within the well and atmospheric gas introduced during sampling.

However, when gas samples were collected at elevated pressures (~50–600 psi), the concentrations and isotopic compositions of the major constituents are similar to those measured in the comingled stream from the Dover 36 CPF or from the injection well, indicating that there is little evidence of isotopic exchange between the injected CO_2 and the carbonate minerals in the reef over the duration of the sampling period. Nonetheless, there are small but systematic differences in the gas compositions over time that are probably due to mixing of the injected gas with the CO_2 gas that was in the reef at the beginning of the geochemical survey (Fig. 2).

Results of the analyses for replicate samples L-M 5–33 #1, #2, and #3 collected in November 2012 are similar; the samples consist primarily of CO_2 , ~94%, with the remainder consisting of low molecular weight ($\text{C}_1\text{--C}_5$) hydrocarbons. The mean of the $\delta^{13}\text{C}_{\text{CO}_2}$ from well 5–33 was slightly higher than the CO_2 gas from either the high purity stream or the co-mingled stream, ~20.8‰ compared to 20.48‰ and 20.56‰. Gas samples collected in August, October and December 2013 from the L-M 5–33 well were collected at higher pressure, ~300 to 600 psi. These samples contained slightly higher CO_2 concentrations, approximately 96% with a mean $\delta^{13}\text{C}_{\text{CO}_2}$ of 20.39‰ which more closely matches the isotopic composition of the injected gas (Fig. 2). The small increase in CO_2 concentration and decrease in the $\delta^{13}\text{C}$ of CO_2 could reflect mixing and dilution with the injected gas, or reactions with the carbonate minerals in the reef. The $\delta^{18}\text{O}$ of CO_2 is notably different than

that measured for the injected gas, and with the exception of an anomalously high value of ~10‰ for the gas sample collected in Oct 2013, shows a small but systematic decrease from a mean of 4.97‰ (November 2012), to 3.82‰ (December 2013). The shift in $\delta^{18}\text{O}$ of CO_2 could reflect mixing and dilution of the baseline gas sample with the lower $\delta^{18}\text{O}$ of CO_2 in the injection gas, dissolution and partitioning of CO_2 into the oil, or oxygen isotopic exchange with the brine samples over time.

The methane concentrations and isotopic compositions of the higher pressure gas samples from the L-M 5–33 well are similar, although slightly more variable, than those measured in the injection well. Methane concentration ranges from ~1 to 3%, with $\delta^{13}\text{C}_1$ ranging from –50.0‰ to –51.8‰ and δD of –261‰ to –277‰. These values fall within the range previously reported for Antrim Shale methane (Martini et al., 1996).

The isotopic compositions and concentrations of gas collected from the L-M 2–33 monitoring well are extremely variable, likely due to difficulties in collecting representative gas samples from this low pressure well. Two of the samples, collected in August and December 2013, clearly represent contamination with an atmospheric signature. In addition, samples collected in May and July 2013 are composed primarily of CO_2 , yet they also contain significant amounts of N_2 , Ar and O_2 , indicating that air was either present in the well head or had leaked into the sample cylinder. The L-M 2–33 gas sample from October 2013 was distinct in that there was sufficient pressure in the well to allow the well to vent through the sample cylinder for several minutes. This sample has a composition that is similar to those measured from the Dover facility and other wells; it is composed of ~98% CO_2 . However, the $\delta^{13}\text{C}_{\text{CO}_2}$ measured in the L-M 2–33 well is significantly lower than the other sites, ranging from 18.12 to 18.75‰, suggesting that either reactions in the reef or in the well casing are changing the isotopic composition, that the CO_2 is mixing with an *in situ* source that has a different composition, or that the injected CO_2 does not enter the L-M 2–33 monitoring well. Gas from this well typically contains H_2 , suggesting that anaerobic microbial reactions with metals in the well casing may be contributing to the gas chemistry.

3.1.3. Charlton 19 (El Mac Hills) wells

The concentration and isotopic composition of the gas samples collected from the Charlton 19 wells were substantially different than those of the Dover 33 reef or CPF (Table 1). The gas composition of the three samples varied, but were dominated by hydrocarbons-including methane, ethane and propane, with only trace amounts of CO_2 . The isotopic composition of the methane for the EMH samples was similar to those of the Dover 33 reef, with $\delta^{13}\text{C}_{\text{CH}_4}$ ranging from –50.13‰ to –50.57‰ and δD of –268‰ to –286‰. There was insufficient CO_2 in the Charlton 19 samples to determine isotopic composition. The gas composition of the Charlton 19 samples was similar to the average composition for eight fields for Michigan Silurian reefs reported by Charpentier (1989), with ~90% short chain alkanes ($\text{C}_1\text{--C}_3$) and only trace amounts of N_2 and CO_2 . The difference between the gas composition in the Charlton 19 Reef (dominated by alkanes) and the Dover 33 Reef (dominated by CO_2) suggests that the geochemistry of the Dover 33 reef has been dominated by the long-term injection of CO_2 that occurred for approximately 17 years prior to the current study.

3.2. Brine isotopic composition-dissolved inorganic carbon (DIC)

The concentration and isotopic composition of DIC can be used to evaluate the extent of CO_2 dissolution into the brine and subsequent water-rock interactions (Becker et al., 2011; Mayer et al., 2015; Myrtilinen et al., 2010). Five fluid samples from L-M 1–33, L-M 2–33, and L-M 5–33 wells, obtained in October and November of 2012 (before the start of the injection tests), and L-M 2–33 swab samples from October and December 2013, were analyzed several times under different conditions to determine $\delta^{13}\text{C}$ of DIC. Fig. 3 shows that the $\delta^{13}\text{C}$ of DIC

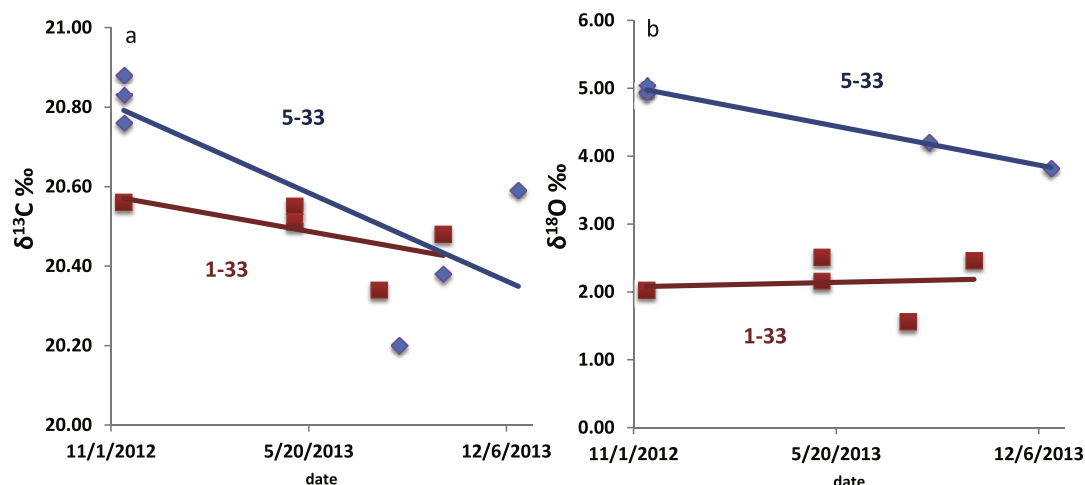


Fig. 2. $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ of CO_2 for the injected gas (either L-M 1–33 or Dover 36 comingled sample, red) and L-M 5–33 monitoring well (blue). Changes over time reflect mixing/dilution of gas in Dover 33 reef at the beginning of the study with gas injected during the course of the geochemical survey.

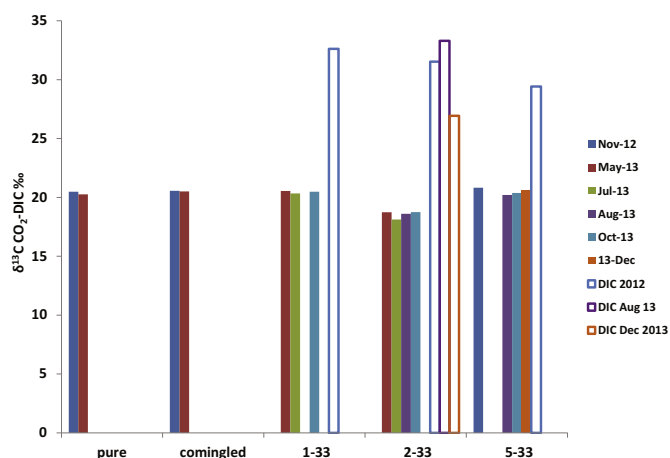


Fig. 3. $\delta^{13}\text{C}$ of CO_2 in gas (solid bars) and DIC in fluids (open) for samples collected from the Dover 36 CPF and the L-M 1–33, L-M 2–33 and L-M 5–33 wells. Differences between fluid and gas may reflect non-equilibrium fractionation of $\delta^{13}\text{C}$ between the gas and fluid or long term microbial methanogenesis.

for these samples are isotopically enriched, ranging from ~ 27 to 33‰ . However, these samples likely degassed during collection (the brine sample from the L-M 5–33 well collected in November 2012 was notably effervescent), which could result in loss of the total dissolved CO_2 either as ^{13}C depleted CO_2 gas, or precipitation of carbonate minerals from the change in pH. Both of these processes, particularly the loss of CO_2 gas, could result in fractionation of the isotopic composition, leading to an increase in the measured $\delta^{13}\text{C}_{\text{DIC}}$. However, a comparison between a SrCO_3 precipitated sample and DIC from a fluid sample indicate that these changes would be less than 4‰ .

A fractionation effect occurs during the dissolution of CO_2 gas into a fluid that is dependent on temperature and speciation (Becker et al., 2011, 2015; Clark and Fritz, 1997; Mayer et al., 2015; Myrntinen et al., 2012a,b). Geochemical analysis of the brine samples indicate that the DIC is predominately bicarbonate (HCO_3^-) (Table 2). The differences between the $\delta^{13}\text{C}_{\text{DIC}}$ and $\delta^{13}\text{C}_{\text{CO}_2}$ gas in these samples are approximately $9\text{--}12\text{‰}$, greater than the expected fractionation values of about $6\text{--}8\text{‰}$ for equilibrium between CO_2 gas and dissolved bicarbonate species at reservoir conditions, approximately 35°C (Becker et al., 2011; Mayer et al., 2015; Myrntinen et al., 2012a,b). However, given that the CO_2 speciation calculations (see Geochemical Modelling section) indicate that solution speciation is dominated by dissolved CO_2

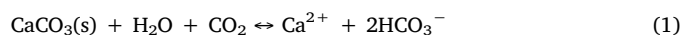
gas (H_2CO_3) and not HCO_3^- , the predicted fractionation between DIC and CO_2 gas should be lower, $\sim -1\text{‰}$ (Becker et al., 2011; Mayer et al., 2015; Myrntinen et al., 2012a,b), thus $\delta^{13}\text{C}$ of DIC in equilibrium with the injected CO_2 should have a $\delta^{13}\text{C}$ value of about $19.5\text{--}20\text{‰}$.

Considering the limited number of samples that were collected, and the possibility of sample outgassing that could change the isotopic composition, it is not clear whether the $\delta^{13}\text{C}_{\text{DIC}}$ collected from the wells reflect a non-equilibrium fractionation between $\delta^{13}\text{C}$ of CO_2 and DIC, or if the isotopically elevated $\delta^{13}\text{C}$ of DIC is controlled by the long term *in situ* microbially mediated methanogenesis within the reef structure. Also notably, the fluids from the L-M 1–33 and L-M 5–33 wells were collected near the beginning of the study, before the majority of the CO_2 was injected in the current study, thus these samples could reflect prior CO_2 flooding that occurred in the decades before the injection tests. In addition, the $\delta^{13}\text{C}_{\text{DIC}}$ of the Dover 33 brine was significantly higher than those measured from a fluid sample obtained from the Fieldstone 2–33 well (an adjacent lobe of the reef) with $\delta^{13}\text{C}_{\text{DIC}}$ of $\sim 5.5\text{‰}$.

Martini et al. (1996, 2003, 2008) report similar $\delta^{13}\text{C}_{\text{DIC}}$ from the Antrim Shale brine ($\sim 25\text{--}30\text{‰}$) which they attribute to microbially mediated reduction of CO_2 to produce methane. The difference between the isotopic composition of CO_2 and methane $\Delta_{\text{CO}_2\text{--CH}_4}$ is $\sim 70\text{‰}$, which falls within the expected range of isotopic compositions for both biogenic and thermogenic methane production (Clark and Fritz, 1997; Martini et al., 1996, 2003, 2008; McIntosh et al., 2004) suggesting that *in situ* methanogenesis could exert some control on the $\delta^{13}\text{C}_{\text{DIC}}$ in the Dover 33 Reef.

Reactions between the injected CO_2 gas and carbonate minerals within the reef could also impact the $\delta^{13}\text{C}_{\text{DIC}}$ and be used to predict the extent of water-rock interaction (Myrntinen et al., 2010, 2012a,b). Although the isotopic composition of carbonate samples from the reef structure were not measured in this study, the isotopic composition of carbonate rocks from Niagaran pinnacle reefs from the Michigan Basin have been reported (Cercione and Lohmann, 1987; Coniglio et al., 2003). For example, these authors noted significant variation in $\delta^{13}\text{C}$ between host rock and secondary calcite and dolomite cements. Nonetheless, the range in the $\delta^{13}\text{C}$ of the carbonates in their study was only $\sim 0\text{--}6\text{‰}$.

Carbonate mineral dissolution by dissolved CO_2 and isotopic compositions of the CO_2 species can be described by equation (1).



$$\delta^{13}\text{C} \sim 0 - 6\text{‰} \quad \delta^{13}\text{C}_{\text{CO}_2} \sim \delta^{13}\text{C}_{\text{DIC}} \sim 10 - 13\text{‰}$$

Therefore, reactions between injected CO_2 and the reef carbonates should produce $\delta^{13}\text{C}_{\text{DIC}}$ with values intermediate between those of

Table 2
Brine composition from the Dover 33 reef.

Analyte	Analytical Result								Fieldstone 2–33 1	Fieldstone 2–33 2
	LM 1–33 12/10/11	LM 1–33 12/10/23	LM 2–33 12/11/7	LM 2–33 12/8/21	LM 2–33 13/12/16	LM 5–33 12/11/14	LM 5–33 13/8/23			
Ba (mg/L)	0.606	0.800	0.382	0.402	0.776	0.332	1.370	nd	nd	
B (mg/L)	298	265	273	293	303	275	91.9			
Ca (mg/L)	95,200	86,400	84,900	88,800	87,500	99,400	47,100	72,600	71,900	
Fe (mg/L)	243	55	156	654	52	117	1500	130	170	
Li (mg/L)	na	na	na	80.4	77.3	na	57	100	100	
Mg (mg/L)	11,200	9980	10,900	10,700	11,000	8060	8550	7990	7990	
Mn (mg/L)	4.43	1.72	2.88	9.15	3.95	2.20	21.5			
K (mg/L)	18,400	16,200	17,700	17,000	18,000	18,100	6350	12,700	12,700	
Si (mg/L)	23.5	18.6	5.90	1.94	2.04	13.6	5.0	nd	nd	
Na (mg/L)	19,000	16,200	19,100	14,400	21,300	15,900	3450	22,500	21,900	
Sr (mg/L)	3470	3080	3210	3310	3270	3700	1470	2660	2740	
pH	4.10	4.62	4.62	4.33	4.87	4.38	6.09	na	na	
TDS (g/Kg)	380	411	395	398	450	402	183	367	369	
Cl (mg/L)	267,000	251,000	253,000	255,000	261,000	274,000	115,000	246,000	249,000	
Br (mg/L)	ND	2720	2950	2800	2800	3250	< 0.10	2640	2650	
SO ₄ (mg/L)	134	150	126	44	45	143	424	97	97	
F (mg/L)	0.30	0.34	0.34	0.22	0.24	0.32	0.77	3.9	3.4	
DIC (mg/L)	47	83	75	< 200	47	110	ND			
Alkalinity – HCO ₃ (mg/L)	357	631	515	< 9.0	259	785	951			
Specific Gravity	1.29	1.28	1.28	1.29	1.29	1.27	1.12			
Charge Balance (%)	–3.80	–6.67	–5.50	–6.04	–5.20	–11.81	2.48			

carbonate minerals and the injected CO₂ gas (Becker et al., 2011; Mayer et al., 2015). Expected values of $\delta^{13}\text{C}_{\text{DIC}}$ from this reaction would be approximately 10–13‰, which is about 20‰ less than those measured in this study. This is consistent with little interaction between the injected gas and the carbonates in the reef over the course of the study.

Cercone and Lohmann (1987) conducted a study on the diagenetic alteration of a Northern Michigan Niagaran pinnacle reef structure. Their results show that the reefs have experienced a complex diagenetic history that is evident in the host rock and carbonate cements. Cercone and Lohmann (1987) concluded that the mineralogy and isotopic composition of the cement precipitates reflects the isotopic composition of regional fluids that infiltrated the reef structure, and that these fluids did not equilibrate with the host rock in the reef structure. This suggests that the *in situ* brines did not undergo extensive water-rock interaction with the reefs over geologic time.

3.3. Water isotopes: CO₂ interaction

Four brine samples were analyzed for $\delta^{18}\text{O}$ and δD to determine the source of the water and interactions among the brine, gas and surrounding rock. Results are listed in Table 3 and plotted in Fig. 4.

Values for δD and $\delta^{18}\text{O}$ of brine samples from the L-M 2–33 and L-M 5–33 monitoring wells are similar, however, the isotopic composition of water from the L-M 1–33 injection well is substantially different. The data plot below the global meteoric water line, which is typical for sedimentary basin brines, indicating that the water is not of recent meteoric origin, although it could have evolved from older meteoric

Table 3

Isotopic composition of brine samples, L-M 1–33, L-M 2–33, and L-M 5–33, from October and November of 2012, and a L-M 2–33 swab sample from October 2013.

Sample ID	Date Collected	$\delta\text{D H}_2\text{O}$ (‰)	$\delta^{18}\text{O H}_2\text{O}$ (‰)
L-M 1-33	10/11/12	–130.3	–7.98
L-M 2-33	11/07/12	–72.2	–2.75
L-M 2–33 (Dup)	11/07/12	–76.2	–3.68
L-M 2-33-33A	08/21/13	–77.4	–4.45
L-M 2-33-33B	08/21/13	–80.3	–3.81
L-M 5-33	11/12/12	–65.9	–4.49

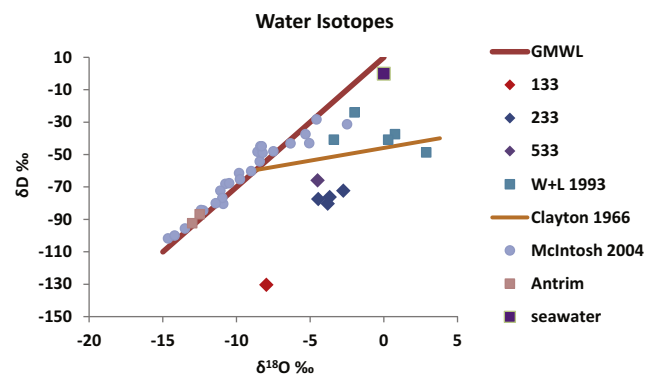


Fig. 4. Global meteoric water line (GMWL) and $\delta^{18}\text{O}$ and δD for brine samples from the L-M 1–33, L-M 2–33 and L-M 5–33 wells, with other Michigan basin brines and seawater for comparison (Clayton et al., 1966; Wilson and Long, 1993a,b (W + L); McIntosh et al., 2004). Antrim data are from McIntosh et al. (2004).

fluids (Clayton et al., 1966). The isotopic composition of brine from the monitoring wells (L-M 2–33 and L-M 5–33) from the Dover 33 reef are similar to those reported for other Michigan Basin brine samples (Hobbs et al., 2008; McNutt et al., 1987; Wilson and Long, 1993a,b), though the values for the L-M 2–33 and L-M 5–33 wells plot slightly below the line originally described by Clayton et al. (1966) for Michigan Basin samples. Brine samples exhibit a relative enrichment in ^{18}O compared to local meteoric water which could be indicative of oxygen isotopic exchange between water and either CO₂, carbonate minerals or the input of hydration waters from evaporites (Golding et al., 2013; Johnson et al., 2011a; McNutt et al., 1987; Wilson and Long, 1993a,b). The isotopic composition of water measured from the L-M 1–33 injection well is significantly different than water from the two monitoring wells, and from other published values from Michigan basin brines. Relatively low δD values may reflect some contribution from Antrim shale brine or hydrocarbon, or recent meteoric water that was injected to enhance oil recovery prior to the current study (Golding et al., 2013; Martini et al., 1996; McIntosh et al., 2004). Although the $\delta^{18}\text{O}$ of the L-M 1–33 brine is also more negative compared to the brines in the monitoring wells, it appears to be impacted by the injected CO₂ (Fig. 4).

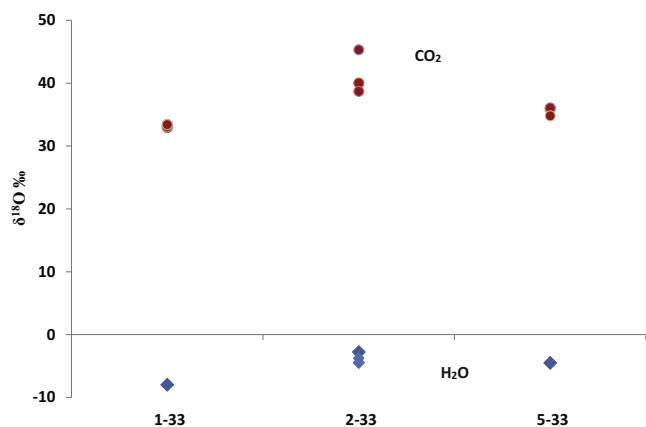
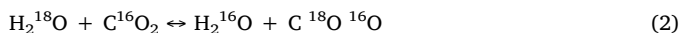


Fig. 5. $\delta^{18}\text{O}$ in CO_2 (recalculated with respect to VSMOW) in gas (red) and $\delta^{18}\text{O}$ in H_2O for water (blue) isotopes in the L-M 1–33, L-M 2–33 and L-M 5–33 wells. $\delta^{18}\text{O}$ co-varies between the water and gas samples for the L-M 1–33 and L-M 5–33 wells suggesting isotopic exchange between the CO_2 and H_2O .

Although there is little variation observed in the $\delta^{13}\text{C}_{\text{CO}_2}$ between the injection and monitoring wells, the $\delta^{18}\text{O}_{\text{CO}_2}$ of the monitoring wells is ~ 2 – 12 ‰ greater than that of the injected gas (Table 1), and co-varies with the $\delta^{18}\text{O}_{\text{H}_2\text{O}}$ suggesting isotopic exchange between the gas and the brine (Fig. 5). The $\delta^{18}\text{O}$ of CO_2 and H_2O for the L-M 1–33 well and the L-M 5–33 well co-vary, ~ 10 ‰ with respect to VPDB and VSMOW, or ~ 39 ‰ when the $\delta^{18}\text{O}$ values for both water and CO_2 are normalized to the VSMOW isotopic scale. These values are close to the expected equilibrium fractionation between CO_2 and water at reservoir conditions, 38.6 ‰ at ~ 35 °C, suggesting ‘equilibrium’ isotope exchange between oxygen in CO_2 and H_2O (eq (2)) (Becker et al., 2011, 2015).



There is considerably more variability between the $\delta^{18}\text{O}$ of CO_2 and H_2O in the L-M 2–33 monitoring well. Differences between the mean oxygen isotopic composition of the H_2O in the brine and CO_2 in the gas phase ranges from approximately 41 to 47.5 ‰ when $\delta^{18}\text{O}$ (VSMOW), suggesting that the CO_2 in the well was not in equilibrium with the brine. However, as mentioned above, the gas collected from the L-M 2–33 well shows considerable variability in both concentration and isotopic composition, with evidence of reactions with the well casing and contributions from atmospheric gas. These gas samples are also collected at low (\sim atmospheric) pressure, and sometimes with insufficient pressure at the well head to flush the gas cylinder. Therefore, the gas collected may have had limited contact with the formation water in that well.

3.4. Sr isotopic composition

Strontium concentrations and isotopic compositions ($^{87}\text{Sr}/^{86}\text{Sr}$) were measured on brine samples collected from the L-M 1–33 injection well and the L-M 2–33 and L-M 5–33 monitoring wells near the beginning of the injection study as well as for the brine sample collected from the Fieldstone 2–33 well. The $^{87}\text{Sr}/^{86}\text{Sr}$ of the brines from the monitoring wells were 0.708647 ± 0.00007 and 0.708649 ± 0.00009 , respectively, while the brine collected from the injection well was slightly more radiogenic 0.708689 ± 0.00010 . These values fall within the range reported for other Silurian Niagaran Reefs which range from 0.70845 to 0.70910 (Coniglio et al., 2003) and are consistent with Middle Silurian seawater composition (Azmy et al., 1999; Coniglio et al., 2003). The Sr isotopic composition of the injection well brine may reflect reactions with minerals containing more radiogenic Sr (such as clays) as a result of CO_2 injection during the study period or during previous flooding events. Alternatively, this

difference may reflect the variability of Sr isotopic composition in the reef structure because a similar $^{87}\text{Sr}/^{86}\text{Sr}$ ratio was measured in the brine sample from the adjacent reef lobe.

3.5. Geochemical modelling

Most of the brine samples were collected near the beginning of the current study, though it was possible to collect fluid samples from the L-M 2–33 well throughout most of the injection experiment. Additional brine samples from an adjacent lobe of the reef (Fieldstone 2–33) were collected after the CO_2 injection experiment for comparison to the samples collected in the main reef structure (Table 2). The water samples are Ca–Na–Cl brines with a total dissolved salt content (TDS) of ~ 400 g/L. With the exception of one sample collected from a holding tank downstream from the L-M 5–33 well (at Dover 36 CPF) on 8/23/13, the compositions of the water samples are similar; concentrations of major constituents vary by less than 20% among samples. Salt composition and concentrations from this site are similar to those reported for the Michigan Basin and Niagaran Reefs (Kharaka and Hanor, 2007; McNutt et al., 1987; Wilson and Long, 1993a,b).

Geochemical modelling of hypersaline brines is difficult because many modelling programs or thermodynamic databases are not adequate for calculating element speciation or mineral saturation at elevated salinities (Appelo, 2015; Appelo et al., 2014; Bethke and Yeakel, 2013; Rowland et al., 2015). Therefore, several approaches were used to characterize geochemical parameters of these brines. The first step was to use measured brine composition and calculate speciation and mineral saturation index for conditions near the start of the current injection experiment, and for samples from the L-M 2–33 well that were collected during the injection. The second step involved two different predictive modelling approaches to determine how CO_2 solubility, brine composition and mineral solubility would evolve as CO_2 is injected into the reef structure.

3.5.1. Initial conditions

Geochemical modelling of brine composition and mineral saturation was done on initial measured brine compositions using two software programs, Geochemists Workbench (GWB version 8) and PHREEQC Interactive (Version 3.1.7.9213). The Pitzer data base and major element concentrations (B, Ca, Fe, Mg, K, Na, Sr, pH, Cl, SO_4^{2-} and HCO_3^- alkalinity from Table 2) were used as input for the models. Because the results of these calculations were similar for the two modelling programs, only Saturation Index data (SI) calculations from PHREEQC are presented (Table 4). The results from model output for samples L-M 2–33 collected August 2103 and December 2013 are omitted because the model would not converge on a solution for the measured compositions. Data for the L-M 5–33 sample collected on August 2013 were not used because this sample was collected from a tank at the Dover 36 CPF and therefore is not representative of the reservoir fluid. Given the uncertainties in these modelling calculations, if the calculated SI for a phase is within ± 0.5 , the solution is considered to be saturated with respect to that phase.

Results of the initial SI calculations suggest that brines are super-saturated with respect to carbonate minerals (calcite SI ~ 3.4 to 4 ; aragonite SI ~ 3.2 to 3.8 , dolomite SI ~ 6.7 to 7.8) in the reef structure, thus the model predicts that these phases are thermodynamically favored to precipitate from solution. Brine samples are also super-saturated with respect to sulfate minerals (gypsum, anhydrite and celestite), and halite indicating that these minerals should also precipitate within the reef. The modelling results show samples are saturated with respect to sylvite (KCl) suggesting equilibrium with sylvite (KCl) may be controlling the potassium concentration within the brine. The results also show that other phases, such as boric acid, carnallite, and nahcolite are approaching saturation in these brines (Table 4).

Table 4
Saturation Index (SI) for selected minerals calculated using PHREEQC.

Mineral name	Composition	L-M 1–33	L-M 1–33	L-M 2–33	L-M 5–33
		12/10/ 11	12/10/ 23	12/11/ 07	12/11/ 14
Anhydrite	CaSO ₄	1.64	1.31	0.99	1.66
Aragonite	CaCO ₃	3.21	3.40	3.21	3.82
Arcanite	K ₂ SO ₄	−4.60	−4.40	−4.34	−4.55
Bischofite	MgCl ₂ ·6H ₂ O	−1.81	−2.21	−1.82	−2.00
Borax	Na ₂ (B ₄ O ₅ (OH) ₄)·8H ₂ O	−6.03	−5.96	−5.62	−5.84
Boric acid, s	B(OH) ₃	−0.60	−0.78	−0.75	−0.65
Brucite	Mg(OH) ₂	−5.68	−5.23	−5.93	−5.33
Calcite	CaCO₃	3.38	3.57	3.40	3.99
Carnallite	KMgCl ₃ ·6H ₂ O	−0.70	−1.29	−0.74	−0.90
Celestine	SrSO ₄	2.12	1.74	1.45	2.09
CO ₂ (g)	CO ₂	1.85	1.66	1.34	1.94
Dolomite	CaMg(CO₃)₂	6.71	7.08	6.76	7.75
Epsomite	MgSO ₄ ·7H ₂ O	−4.41	−4.15	−3.84	−4.52
Glauberite	Na ₂ Ca(SO ₄) ₂	−1.27	−1.85	−1.82	−1.39
Gypsum	CaSO₄·2H₂O	0.97	0.81	0.73	1.00
Halite	NaCl	0.72	0.31	0.53	0.62
Magnesite	MgCO ₃	2.22	2.39	2.52	2.64
Mirabilite	Na ₂ SO ₄ ·10H ₂ O	−7.00	−6.37	−5.72	−7.02
Nahcolite	NaHCO ₃	−0.54	−0.45	−0.62	−0.26
Natron	Na ₂ CO ₃ ·10H ₂ O	−8.78	−7.63	−7.89	−8.20
Nesquehonite	MgCO ₃ ·3H ₂ O	−1.65	−1.21	−1.08	−1.19
Pentahydrate	MgSO ₄ ·5H ₂ O	−3.98	−3.90	−3.81	−4.11
Sylvite	KCl	−0.08	−0.27	0.06	−0.09
Thenardite	Na ₂ SO ₄	−3.25	−3.50	−3.48	−3.38
Trona	Na ₃ H(CO ₃) ₂ ·2H ₂ O	−6.53	−5.99	−6.20	−5.75

3.5.2. Predictive modelling

Two different modelling approaches were employed in order to determine how the composition of the brine might evolve as CO₂ gas is injected into the reef structure. The first predictive model involved calculating CO₂ solubility over a range of temperatures and pressures in the brines and then using these CO₂ concentrations and brine compositions to determine mineral solubility (Duan et al., 2006 and GWB). The second modelling approach allowed brine to react with a fixed amount of CO₂ over a range of pressure (PHREEQC). Because the brine compositions are similar in the three wells, only two brine compositions were selected as a basis for the subsequent geochemical calculations for predictive modelling, the L-M 1–33 sample from October 2012 and the L-M 5–33 sample from November 2012. These two samples were collected close to the start of the CO₂ injection experiment and thus are most representative of the initial reef conditions for the current geochemical assessment.

In order to determine the potential for CO₂ to dissolve into solution (solubility trapping) under reservoir conditions, ~35–40 °C (Kelley et al., 2014), we used an average brine composition (from the L-M 1–33 and L-M 5–33 above) and the model of Duan et al. (2006). This model was developed to calculate CO₂ solubility in brines containing Na, K, Ca, Mg, Cl, and SO₄ over a range of temperature and pressure (Fig. 6).

Predicted CO₂ solubility increases with increasing pressure, although there is a marked change in the slope of CO₂ solubility around 100–200 bar (Fig. 6). There is little difference in the calculated CO₂ solubility between 35 °C and 100 °C, suggesting that changes in pressure rather than temperature are more important in controlling CO₂ storage in this system. Zhao et al. (2015) report similar but slightly higher values for CO₂ solubility from their model of a synthetic Michigan Basin brine, with CO₂ concentrations ranging from ca 0.54–0.60 mol/kg at 50 °C, and 0.38–0.50 mol/kg at 100 °C over a pressure range of 100–200 bar. The calculated CO₂ solubility concentrations are substantially higher than the measured DIC or alkalinity for all samples in this study (Table 2). Although some uncertainty exists with respect to the measured dissolved total CO₂ concentrations due to the fact that the samples could have degassed during collection, the maximum measured dissolved CO₂ for the brines was only ~0.013 M (L-M 5–33 well). This

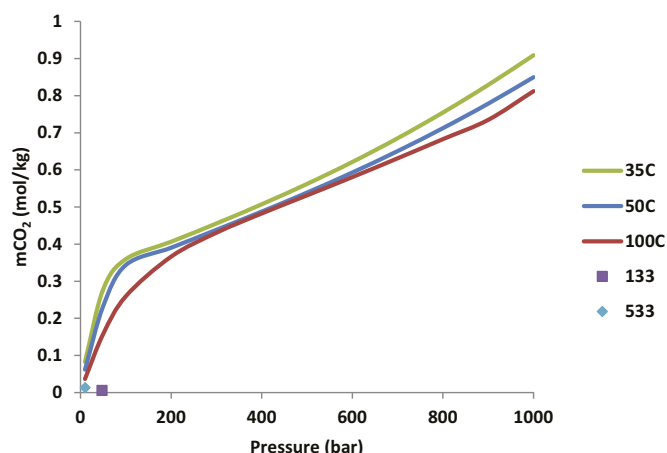


Fig. 6. Predicted CO₂ solubility (mole/kg) for a typical Dover 33 well brine composition at 35, 50 and 100 °C based on the model of Duan et al. (2006). Measured total CO₂ and pressure at the well head for the L-M 1–33 and L-M 5–33 wells are plotted for comparison. For this range of T there is little difference in solubility, suggesting pressure is more important for controlling CO₂ storage.

is only about 20% of the concentration predicted (~0.062 M) for this sample based on pressure measured at the well head, ~0.062 M. Results of CO₂ solubility modelling suggest that there is potential for considerable CO₂ storage dissolved in the brine. However, calculations from the Duan et al. (2006) model do not consider other physical or chemical factors, such as the dissolution rate of CO₂ gas into the brine, diffusion rate of CO₂ in solution, the speciation of CO₂ in solution, or reaction rate of CO₂ with carbonate minerals.

CO₂ solubility values generated from the Duan et al. (2006) model, the initial brine composition from the L-M 1–33 and L-M 5–33 wells, and an estimated reservoir temperature of 50 °C were used as inputs for subsequent geochemical modelling using Geochemists Workbench (GWB), to simulate the effect of increasing CO₂ on brine composition and mineral dissolution-precipitation reactions. Results of these calculations show that brines are supersaturated (saturation index > 0) with respect to calcite and dolomite (Fig. 7), indicating that there should be no net dissolution of the carbonate minerals in the reef, consistent with the results of the CO₂ gas and DIC isotopic compositions. Model calculations do indicate however, that saturation indices, and pH, would decrease with increasing CO₂ injection. The pH values predicted by these models range from ~4.5 to 5.5, suggesting that the DIC speciation should be dominated by dissolved CO₂ gas (H₂CO₃). The pH predicted by the geochemical calculations is approximately 1 pH unit higher than the measured pH (Fig. 7).

The second predictive model approach was to determine the potential for CO₂ solubility trapping and the evolution of brine composition with increased CO₂ injection using the geochemical program PHREEQC (Version 3.1.7.9213, released Jan 2015). This version of the software incorporates additional thermodynamic data for calculating gas solubility and mineral reactions for the elevated temperature, pressure, and salinity conditions typically encountered in CCUS sites (Appelo et al., 2014; Appelo, 2015).

This approach differs from the original calculations based on GWB in that pH can be calculated from CO₂ solubility and speciation with increasing pressure. This is important because the solubilities of carbonate phases and carbonate speciation are strongly pH dependent. Initial conditions used for these models were similar to those used in the GWB simulations, with the exception of dissolved CO₂ which was calculated by allowing an initial fixed amount of CO₂ (0.5 and 5 mol) to react with 1 L of brine at 50 and 100 °C, over a range of pressure (10–1000 bar). Because the model predictions for the 0.5 and 5 mol CO₂ reactions were similar, only results of the 0.5 mol CO₂ are presented.

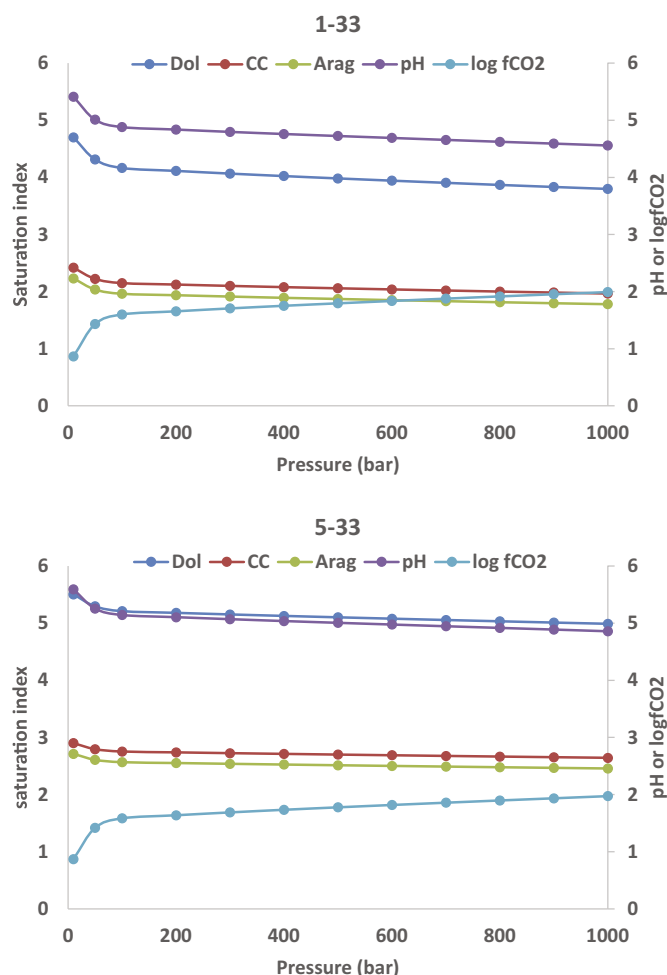


Fig. 7. Calculated saturation index for calcite (CC), dolomite (Dol) and aragonite (Arag), and calculated $f\text{CO}_2$ and pH for brines from the L-M 1-33 (upper diagram) and L-M 5-33 injection wells. Initial brine composition was taken from Table 3, CO_2 solubility was calculated from the model of Duan et al. (2006). Geochemical modelling calculations suggest that brines are super-saturated with respect to carbonate minerals.

Results of the total CO_2 solubility calculations for the L-M 1-33 and L-M 5-33 wells are shown in Fig. 8. The increase in dissolved CO_2 concentrations as a function of pressure are similar for the two brines. The results of the PHREEQC calculations are somewhat different than those predicted from the Duan et al. (2006) model. These small differences are due to differences in input parameters to the models, and differences in how the two models determine activity and fugacity coefficients for different compounds. Below pressures of ~ 300 bar the trends predicted by the two models are similar. However, concentrations predicted by the Duan et al. (2006) model are approximately twofold greater than those by the PHREEQC model. As pressure increases, the Duan et al. (2006) model predicts an almost linear increase in dissolved CO_2 concentration with increasing pressure, whereas the CO_2 concentrations predicted by the PHREEQC model increase only slightly with pressure from 300 to 1000 bar. The maximum CO_2 solubility predicted by the PHREEQC model is only $\sim 30\%$ of that predicted by Duan et al. (2006). Given the current reservoir conditions of $\sim 35^\circ\text{C}$ and 230 bar, predicted CO_2 solubility would be approximately 0.22 M, predominately as H_2CO_3 .

Predictions for the change in carbonate mineral saturation index and pH as a function of pressure from the PHREEQC calculations are presented in Fig. 9 for the L-M 1-33 and L-M 5-33 brines. Although the values predicted from the PHREEQC model differ slightly from those

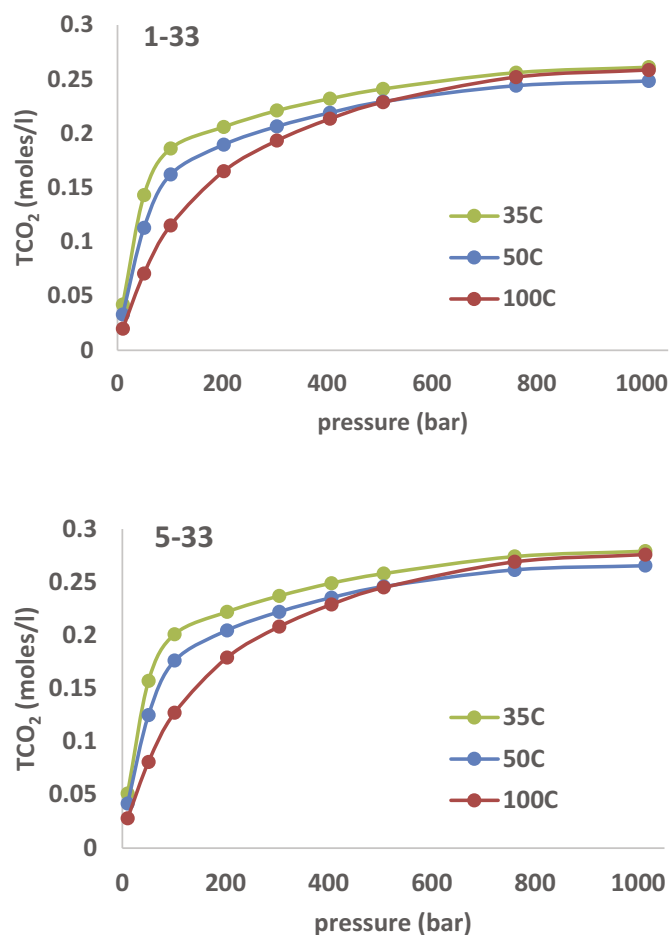


Fig. 8. CO_2 solubility (TCO_2 moles/l) calculated using PHREEQC for the L-M 1-33 (top) and L-M 5-33 wells.

generated by the GWB model, the overall trends from the two geochemical models are similar. Both models indicate that solutions are oversaturated with respect to carbonate minerals and that there is a systematic decrease in SI and pH with increasing pressure as more CO_2 dissolves into the brine. Thus, the modelling results predict that there is significant potential for CO_2 storage by mineral trapping. Even though the calculated total CO_2 concentrations are lower, the pH predicted by the PHREEQC model is approximately 1 pH unit lower as well. The initial pH ranges from ~ 4.9 to 5.2 in the model simulations, and decreases by approximately 1 pH unit. Predicted pH values are similar to the measured values (Fig. 9). These small differences in pH could have implications for reactivity of other mineral phases within the reef structure because solubility and reactivity of most silicate mineral phases are pH dependent. In general, silicate mineral reactivity is independent of pH in the range of ~ 5 –8, and then increases with either increasing or decreasing pH. Therefore, these small changes in pH may promote silicate mineral dissolution within the reef, thereby enhancing porosity and permeability. The current data set from the geochemical results and the geochemical modelling data base are inadequate for predicting silicate saturation states.

4. Summary and conclusions

Gas samples were collected from the Dover 36 CPF, injection well (L-M 1-33), and two monitoring wells (L-M 2-33 and L-M 5-33) over the course of this study. The concentrations and isotopic compositions of major constituents in the injected gas did not vary substantially over time. The gas was composed primarily of CO_2 ($> 95\%$), and CH_4 ($> 2\%$) with trace amounts of other hydrocarbons and nitrogen. The

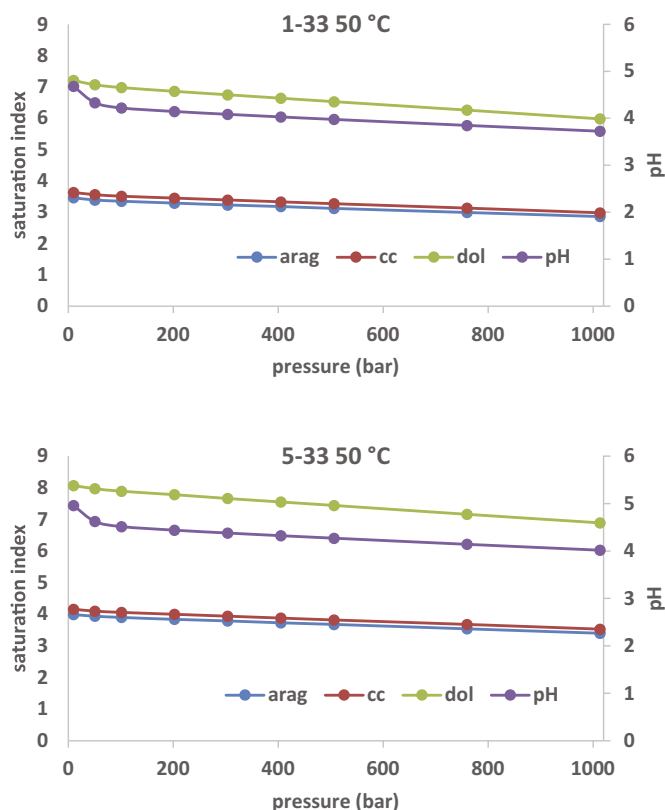


Fig. 9. Carbonate mineral saturation index and pH predicted for the L-M 1-33 and L-M 5-33 wells using PHREEQC.

mean values of $\delta^{13}\text{C}$ for CO_2 and CH_4 are 20.5‰ and −52.0‰ respectively, which is consistent with published data on Antrim shale gas, the source of the CO_2 used in the EOR.

The concentrations and isotopic compositions of the gas samples collected at the L-M 2-33 and L-M 5-33 monitoring wells varied substantially, however much of this variation was attributed to sampling difficulties at the well head, especially for samples collected at low pressure (~atmospheric). Higher pressure gas samples (> 50 psi) from the L-M 5-33 well had concentrations and isotopic compositions very similar to those of the injected gas, indicating that there was little evidence of isotopic exchange between the gas and the carbonate minerals in the reef. However, there was a small but systematic shift in the $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ of CO_2 in the L-M 5-33 well towards the isotopic composition of the injected gas reflecting mixing and dilution with the gas in the reef at the beginning of the study.

Gas samples from the L-M 2-33 monitoring well were collected at low (~atmospheric) pressure. Concentrations and isotopic compositions of gas samples from the L-M 2-33 well were distinctly different from both the L-M 1-33 injection well and the L-M 5-33 monitoring well, commonly exhibiting signatures that are consistent with an atmospheric signal or with reactions within the well casing. The $\delta^{13}\text{C}$ values of CO_2 measured at this well were consistently lower (~18.5‰) and may reflect conditions in the reef prior to the large scale CO_2 injection.

Samples of the reservoir brine were collected from the L-M 1-33, L-M 2-33, and L-M 5-33 as part of this study. The $\delta^{13}\text{C}_{\text{CO}_2}$ of DIC for the brine samples are relatively positive ~27–33‰, or approximately 9–12‰, greater than the $\delta^{13}\text{C}_{\text{CO}_2}$ gas in the wells suggesting that either the DIC is not in equilibrium with the CO_2 gas, or that the brine samples degassed during collection, changing both DIC concentration and isotopic composition.

$\delta^{18}\text{O}$ and δD for the L-M 2-33 and L-M 5-33 monitoring wells are similar and plot below the meteoric water line, indicating that the brine

is not of recent meteoric origin. The $\delta^{18}\text{O}$ and δD of the L-M 1-33 well is significantly lower than the other wells, and may reflect some contribution of recent meteoric water, or oxidation of isotopically light hydrocarbon (methane) from the Antrim Shale. The $\delta^{18}\text{O}$ of CO_2 and H_2O in the L-M 1-33 and L-M 5-33 wells co-vary, suggesting near equilibrium isotopic exchange between oxygen in the gas and brine.

Geochemical modelling was used to estimate the potential CO_2 solubility under reservoir conditions and to predict how the composition of the brine would evolve as CO_2 dissolves. Calculations show that the brine is supersaturated with respect to carbonate minerals (calcite and dolomite), and although the modelling results indicate that both SI and pH will decrease with increasing pressure, the fluid will still be supersaturated, indicating the potential for CO_2 trapping in both dissolved and mineral form.

Declarations of interest

None.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.apgeochem.2018.12.008>.

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