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Oxygen isotopes as a tool to quantify reservoir-scale CO₂ pore-space saturation

Sascha Serno¹, Stephanie Flude², Gareth Johnson³, Bernhard Mayer³, Rūta Karolytė³, R. Stuart Haszeldine¹, Stuart M.V. Gilfillan¹

¹ School of GeoSciences, The University of Edinburgh, Grant Institute, The King’s Buildings, James Hutton Road, Edinburgh EH9 3FE, United Kingdom
² Isotope Geosciences Unit, Scottish Universities Environmental Research Centre, Rankine Avenue, East Kilbride G75 0QF, United Kingdom
³ Applied Geochemistry Group, Department of Geoscience, University of Calgary, 2500 University Drive NW, Calgary, Alberta T2N 1N4, Canada

1. Introduction

Carbon Capture and Storage and/or Utilisation (CCS or CCU) involves capturing and purifying carbon dioxide (CO₂), compressing, transporting and injecting it into the geological subsurface, particularly deep saline aquifers, depleted hydrocarbon fields, basalt formations or coal seams. Capture and subsequent geological storage of CO₂ in rock formations is a commercially available means of reducing CO₂ emissions to the atmosphere from fossil fuel combustion for power generation and industrial processes. When combined with the combustion of biomass (BECCS) the technology provides the only currently available negative emissions technology (Scott et al., 2013). Mining of fossil fuels results in the production of CO₂, which is captured and used as a fuel in the production of electricity. This process, known as CO₂ Enhanced Oil Recovery (EOR), is a commercially proven technology for the long-term storage of CO₂. However, it is estimated that only a small fraction of CO₂ emissions can be captured and stored using this method, and the remaining CO₂ must be sequestered in geological formations. The challenges associated with the geological storage of CO₂, such as the identification of suitable reservoirs and the monitoring of the injection and storage processes, are well known (Nicol and Peacock, 2004; Metcalf et al., 2005; Metz et al., 2006). After injection commences, CO₂ is initially stored in sedimentary formations through three different mechanisms: (1) structural trapping, where CO₂ is trapped beneath an impermeable cap rock, (2) residual trapping, the immobilisation of CO₂ through trapping within individual and dead end spaces between rock grains, and (3) solubility trapping, where CO₂ is dissolved into the reservoir water that fills the pores between rock grains. Studies of natural CO₂ reservoirs and CO₂ test injection sites have shown that structural and stratigraphic trapping and residual trapping are almost instantaneous trapping mechanisms, with dissolution trapping requiring more time for the CO₂ to dissolve which varies depending on the amount of CO₂ injected relative to available water and often the presence of an actively recharging aquifer (Scott et al., 2013). Mineral trapping of CO₂ as a result of chemical reactions between the injected CO₂ and the host rock to form new carbonate minerals within the pores is a longer term storage mechanism in sedimentary formations. Depending on the mineralogy of the reservoir rocks, mineral trapping may play a role after a few decades to several hundreds of years after initiation of CO₂ injection (e.g., Audigane et al., 2007; Sterpenich et al., 2009; Xu et al., 2004), though a number of natural CO₂ reservoirs do not show evidence for such trapping (Gilfillan et al., 2008, 2009). Mineral trapping of injected CO₂ can occur more quickly in reactive basaltic rocks and where CO₂ is pre-mixed with water as shown by recent experiments undertaken in Iceland (Matter et al., 2016) and northwest USA (McGrail et al., 2017).

In order to accurately model the long-term fate of CO₂ in the reservoir, it is essential to understand the processes involved in the storage of CO₂ and the factors that control these processes. One of the key challenges in understanding the long-term fate of CO₂ in geological formations is the ability to accurately predict the amount of CO₂ that will be stored and the rate at which it will be stored. This is particularly important for the development of CO₂ storage projects, as it is necessary to ensure that the CO₂ will be stored safely and securely for a sufficient period of time to meet the needs of the future generation.

In this study, we focus on the role of oxygen isotopes in the assessment of CO₂ storage in geological formations. Oxygen isotopes are a natural tracer that can be used to assess the fate of CO₂ in reservoirs, and they have been used extensively in the assessment of CO₂ injection and storage in geological formations. However, the use of oxygen isotopes in the assessment of CO₂ storage is not well understood, and there is a lack of understanding of the role of oxygen isotopes in the assessment of CO₂ storage in geological formations. Therefore, in this study, we assess the advantages and potential limitations of using oxygen isotopes to quantify CO₂ pore-space saturation based on a comprehensive review of oxygen isotope measurements from reservoir waters and various global CO₂ injection test sites. We further summarise the oxygen isotope composition of captured CO₂ in order to establish the controls on this fingerprint.

Keywords:
Oxygen isotopes
CO₂ pore-space saturation
Carbon Capture and Storage
Captured CO₂
Inherent tracer

ABSTRACT

Structural and residual trapping of carbon dioxide (CO₂) are two key mechanisms of secure CO₂ storage, an essential component of Carbon Capture and Storage technology. Estimating the amount of CO₂ that is trapped by these two mechanisms is a vital requirement for accurately assessing the secure CO₂ storage capacity of a formation, but remains a key challenge. Here, we review recent field and laboratory experiment studies and show that simple and relatively inexpensive measurements of oxygen isotope ratios in both the injected CO₂ and produced water can provide an assessment of the amount of CO₂ that is stored by residual and structural trapping mechanisms. We find that oxygen isotope assessments provide results that are comparable to those obtained by geophysical techniques. For the first time we assess the advantages and potential limitations of using oxygen isotopes to quantify CO₂ pore-space saturation based on a comprehensive review of oxygen isotope measurements from reservoir waters and various global CO₂ injection test sites. We further summarise the oxygen isotope composition of captured CO₂ in order to establish the controls on this fingerprint.
injection formation of a commercial-scale CCS project, it is helpful to quantitatively assess the amount of structural, residual and solubility trapping acting on the reservoir scale. Whilst laboratory core flood experiments on samples taken from the injection formation can provide some indication of the degree of CO2 trapping expected (e.g., Krevor et al., 2012, 2015), these are limited to the individual sample and up-scaling the results to the entire reservoir is notoriously difficult. A reservoir-scale short-term test undertaken at the field site prior to large-scale injection can help to reduce the risk and uncertainty in estimating the CO2 storage capacity of a formation and provides a commercial operator with greater reassurance of the viability of their proposed storage site. This is particularly true for two of the CO2 storage mechanisms, structural and residual trapping of CO2, which we combine here with the term “CO2 pore-space saturation”. These two mechanisms can play a major role for CO2 plume migration, immobilisation, storage security and reservoir management (Doughty and Pruess, 2004; Ennis-King and Paterson, 2002; Juanes et al., 2006; Krevor et al., 2015; Qi et al., 2009). Despite the important role of these trapping mechanisms in commercial-scale CCS projects, there is a current lack of cost-effective and reliable methodologies to estimate their extent on the reservoir scale (Mayer et al., 2015). Geophysical approaches to determine CO2 pore-space saturation have a number of limitations, for example thin layers are not resolvable due to seismic resolution (Wells et al., 2006), while well-based geophysical technologies such as pulsed neutron logging are restricted to the region of pore space in the vicinity of the well (~25 cm; Dance and Paterson, 2016).

Stable oxygen isotopes of water and CO2 may be highly suitable for assessing CO2 pore-space saturation (Mayer et al., 2015). As inherent tracers, stable isotopes are relatively inexpensive, particularly when compared to other artificial or added geochemical tracers like noble gases, perfluorocarbon tracers or sulfur hexafluoride. Studies from several CO2 storage sites in Canada (Johnson et al., 2011), the USA (Kharaka et al., 2006) and Australia (Serno et al., 2016), along with laboratory experiments (Barth et al., 2015; Johnson and Mayer, 2011), have shown that the oxygen isotope ratio ($\delta^{18}O$) of reservoir water can change, without a change in the hydrogen isotope composition of the water, due to isotopic equilibrium exchange between the reservoir water and CO2 added to the reservoir. These studies revealed that the change in the $\delta^{18}O$ value of the reservoir water due to oxygen isotope exchange with CO2 under conditions typical for CO2 injection sites can be related to the fraction of oxygen in the system sourced from CO2 (Barth et al., 2015; Johnson and Mayer, 2011; Johnson et al., 2011; Kharaka et al., 2006; Serno et al., 2016). Several studies have consequently provided evidence that this change can be successfully used to assess volumetric saturation of free-phase CO2 in the reservoir (Johnson et al., 2011; Li and Pang, 2015; Serno et al., 2016).

In order to improve the application of oxygen isotopes to quantitatively assess CO2 pore-space saturations on a reservoir scale in future CO2 storage projects, we present a review of findings from several CO2 injection field experiments around the globe using oxygen isotope ratios to quantify CO2 pore-space saturation. Furthermore, we summarise published $\delta^{18}O$ values from captured CO2 as a potential CO2 source for field injection tests and make hypothetical predictions regarding the expected $\delta^{18}O$ values of captured CO2 where current data are unavailable or incomplete.

2. Geothermal background

2.1. Changes in the oxygen isotope ratios of reservoir water

Stable isotope analyses of water commonly measure $^2H/^1H$, as $\delta^{2H}$, and $^{18}O/^16O$, as $\delta^{18}O$, where $\delta$ represents the isotope ratio in ‰ relative to Vienna Standard Mean Oceanic Water (VSMOW):

$$\delta_{\text{sample}} = \left( \frac{R_{\text{sample}}}{R_{\text{VSMOW}}} - 1 \right) \times 1000 \quad (1)$$

$R$ represents the $^{18}O/^16O$ or $^2H/^1H$ ratio of samples and the VSMOW standard. All stable isotope ratios in this manuscript are reported in ‰ relative to VSMOW.

For meteoric water, the source of most waters in sedimentary formations, $^2H$ and $^{18}O$ co-vary with values falling along the meteoric water line (Fig. 1). Changes to this trend result from isotope fractionation (e.g. during evaporation) or addition of other hydrogen and/or oxygen sources with different isotope compositions. Significant sources of oxygen in geological reservoirs, other than the reservoir water, are native CO2 derived from geological processes, dissolved inorganic carbon, oxygen within the molecular structure of hydrocarbons, and oxygen in mineral grains (silicates and carbonates) of the host rock formation (Johnson et al., 2011; Mayer et al., 2015).

The sources of reservoir oxygen are typically in isotopic equilibrium with the reservoir fluid due to fast reaction kinetics of the oxygen isotope system (e.g., Karolyte et al., 2017; Mills and Urey, 1940; Raistrick et al., 2009; Vogel et al., 1970). In most natural environments, the amount of oxygen in reservoir CO2 is negligible compared to that in water, resulting in the reservoir water $^{18}O$ values remaining essentially constant and the $\delta^{18}O$ value of CO2 ($\delta^{18}OCO_2$) approaching that of the water plus the appropriate isotopic enrichment factor between water and CO2 ($\varepsilon_{CO_2-H_2O} \approx 10^3 R_{\text{CO}_2-H_2O}$) at the reservoir temperature (Bottinga, 1968). $\varepsilon_{CO_2-H_2O}$ is reported in ‰ and determined using Eq.
(2), defined by Bottina (1968) and discussed in Friedman and O’Neil (1977):

\[
\varepsilon_{\text{CO}_2-H_2O} = -0.0206 \times \left( \frac{10^4}{T} \right) + 17.9942 \times \left( \frac{10^4}{T} \right) - 19.97
\]

(2)

where T is the reservoir temperature in Kelvin. This equation is valid at atmospheric conditions as well as elevated temperatures and pressures relevant for CCS projects (Becker et al., 2015; Bottina, 1968; Johnson et al., 2011). \( \varepsilon_{\text{CO}_2-H_2O} \) typically varies between 26 and 40% (for reservoir temperatures of 25–120 °C).

Oxygen isotope exchange proceeds readily between CO2 and water, and so injection of large amounts of CO2 into the reservoir will result in an oxygen isotope shift away from formation water baseline values, while δ18H values remain constant (e.g., Clark and Fritz, 1997; Craig, 1963; D’Amore and Panichi, 1985; Johnson and Mayer, 2011; Johnson et al., 2011; Lions et al., 2014). Kampman et al. (2014) suggested that diffusive oxygen isotope exchange on a small scale takes place in minutes so that CO2 and water should be in equilibrium in the pore space. At larger spatial scales, the rate of oxygen isotope exchange varies with salinity and temperature. Léuyer et al. (2009) measured the time taken to attain CO2 – H2O isotopic equilibrium for reservoir waters of varying salinities; they found that waters with 0 g/L total dissolved solids (TDS) achieved isotopic equilibrium within 4 h, while waters with 250 g/L TDS required 12 h. Vogel et al. (1970) established that oxygen isotope equilibrium between CO2 and demineralised water was established within 22 h at 25 °C and faster at higher temperatures. Slightly longer timescales of 4–7 days were measured for establishment of equilibrium between supercritical CO2 and water (Becker et al., 2015; Johnson and Mayer, 2011). In the case of CO2 injection, oxygen isotope equilibrium is thus expected to be attained in a matter of days.

An oxygen isotope shift in reservoir water can also be produced via mineral dissolution contributing oxygen previously bound in mineral lattices to the system, especially for carbonate minerals. However, the contribution of this process to changes in δ18O values of reservoir water is usually small relative to the effect caused by injected CO2 (Johnson et al., 2011); laboratory experiments investigating limestone dissolution in CO2 saturated water at 150 bar and 80 °C, and water-rock ratios 40 times higher than typical for storage reservoirs showed that less than 1% of the limestone mass dissolved (Sterpenich et al., 2009). 2.2. Quantifying CO2 pore-space saturation based on oxygen isotope equilibrium exchange between reservoir water and CO2

A quantitative method to estimate CO2 pore-space saturation, based on changes in the δ18O value of reservoir water in contact with free-phase CO2 was first proposed and utilised by Kharaka et al. (2006) and has been further described and applied by Johnson et al. (2011). During CO2 injection into a storage reservoir, a new major source of oxygen is added to the system in the form of supercritical CO2, and the δ18O water value will start to control the oxygen isotope composition of the water-CO2 system. The δ18O value of reservoir water will start to change from the baseline oxygen isotope value, δ18Owater, towards an end-member scenario where the water has a final value, δ18Owater, lower than that of the CO2 by εδ18Owater. Consequently, both CO2 and water δ18O values will change due to isotopic equilibrium exchange reactions (Barth et al., 2015; Johnson and Mayer, 2011; Johnson et al., 2011; Kharaka et al., 2006; Mayer et al., 2015; Serno et al., 2016). The fraction of oxygen in the system sourced from CO2, \( X_{\text{CO}_2} \), can be estimated using Eq. (3):

\[
X_{\text{CO}_2} = \frac{\delta_{\text{CO}_2} - \delta_{\text{water}}}{\delta_{\text{CO}_2} - \delta_{\text{water}}} = \frac{\delta_{\text{CO}_2} - \delta_{\text{water}}}{\delta_{\text{CO}_2} - \delta_{\text{water}}}
\]

(3)

A subsequent oxygen isotope change of the reservoir water due to injected CO2 requires that the difference in δ18O values between the CO2 and water is different to the isotopic enrichment factor \( c_{\text{CO}_2-H_2O} \). If other significant oxygen sources that may promote oxygen isotope shifts of reservoir water can be ruled out, then any shift in the δ18O value of reservoir water indicates that the water must be in contact with the injected CO2. The magnitude of the shift in δ18Owater can be used to assess the relative contributions from dissolved and free-phase CO2. If reservoir conditions and δ18Owater are known, CO2 solubility can be calculated (Duan and Sun, 2003), along with a theoretical δ18O value of fully CO2-saturated reservoir water. When the δ18O value of reservoir water changes by less than is predicted for maximum CO2 dissolution, then the water is under-saturated and any free-phase CO2 in contact with this water will continue to dissolve (Johnson et al., 2011). A larger δ18O shift than predicted for maximum CO2 dissolution means that the water is over-saturated with CO2, and there is thus a free phase of CO2 (gas, supercritical or liquid) in contact with the water providing excess oxygen to the system. In these circumstances, free-phase (i.e. structurally and residually trapped) CO2 pore-space saturation \( S_{\text{CO}_2} \) can be estimated via Eq. (4), which quantitatively describes the oxygen isotope water-CO2 system:

\[
S_{\text{CO}_2} = \frac{(B X_{\text{CO}_2} + C X_{\text{CO}_2} - B)}{(A-B-A X_{\text{CO}_2} + B X_{\text{CO}_2} + C X_{\text{CO}_2})}
\]

(4)

with A = mol of oxygen in 1 L of free-phase CO2 at reservoir conditions, B = mol of oxygen dissolved in 1 L water from CO2 at reservoir conditions, C = mol of oxygen in 1 L water at reservoir conditions, and \( X_{\text{CO}_2} \) derived from Eq. (3) (Johnson et al., 2011). Eq. (4) was first applied during the Pembina Cardium CO2 Monitoring Pilot in Alberta, Canada, to estimate \( S_{\text{CO}_2} \) (Johnson et al., 2011). In specific field setups when CO2 is co-injected with water/brine, for example during the Otway Stage 2 B experiments, the method can be used to provide an estimate of residual CO2 saturation. This method assumes a closed system and can only be applied if isotopic exchange with minerals in the reservoir, and processes such as gravitational mixing (Riaz et al., 2006) are negligible. Reservoir water may be sampled for oxygen isotope analyses at the wellhead of observation or production wells without being affected by degassing of CO2 since the isotopic equilibrium between water and injected CO2 is established before the CO2 exsolves (Johnson et al., 2011). However, subsequent sample storage should assure prevention of evaporation of water so that its isotopic composition is not altered. Ideally, samples should be collected using a downhole sampling tool like the U-tube sampling system (Freifeld et al., 2005) and, if analysis is not to be completed immediately, with a complete degassing of CO2 at surface to prevent continuous oxygen isotope equilibrium exchange between the water and the incompletely degassed CO2 in the sampling vessel during storage.

2.3. Oxygen isotope laboratory tests assessing CO2 pore-space saturation

Johnson and Mayer (2011) investigated different water-CO2 systems in 150 mL stainless steel cylinders with variable CO2 pressures up to 190 bar (and resulting CO2 concentrations), with CO2 contributing up to 35% of the oxygen in the cylinder. The initial δ18O water value was +0.9‰, and waters with an artificially 18O-enriched δ18O water value of +235.1‰ were used in order to observe changes in the δ18O values of both CO2 and water of several tens ‰. A temperature of 50 °C was used, for which a constant water δ18O of 35.5‰ lower than that of the CO2 was expected when oxygen isotope equilibrium is maintained, and the reaction was undertaken over one week.

The experiments with variable fractions of oxygen sourced from CO2 showed that the larger the increase in the CO2-sourced oxygen fraction (the larger the pressure in the reaction vessel), the larger the decrease in water δ18O from its baseline value towards a value approaching that of the original CO2 plus \( c_{\text{CO}_2-H_2O} \) (Johnson and Mayer, 2011). The oxygen isotope difference between water and CO2 remained constant at 36.4 ± 2.2‰ (1σ, n = 15), identical to the theoretical value of 35.5‰. This suggests that independent of the CO2 concentration,
3. Field applications of oxygen isotope assessments of CO₂ pore-space saturation

3.1. Pembina

During the Enhanced Oil Recovery (EOR) Pembina Cardium CO₂ Monitoring Pilot in the Pembina area west of Edmonton, Alberta (Canada), two phases of CO₂ injection (total of ∼75,000 t of liquid CO₂ trucked to the site and injected in supercritical state) were conducted between March 2005 and March 2008 into the Upper Cretaceous Cardium Formation, a siliciclastic reservoir with sandstones interbedded with shales (Johnson et al., 2011). The measured reservoir temperature was 50 °C and the pressure was ∼190 bar at a depth of ∼1650 m (Hitchon, 2009). The high purity CO₂ injected during the project was delivered by Ferus Gas Industries from three different facilities where the CO₂ was captured from waste gas streams, followed by purification, liquefaction and compression. CO₂ was injected through 2 wells, with 4 observation wells for each of the 2 injection wells (Hitchon, 2009). Two of these observation wells were shared, with an additional 2 off-pattern wells for each injection well being monitored as well. TDS in baseline formation water samples varied between 3.9 and 7.6 g/L for the 8 observation wells (Johnson et al., 2011). Casing gas and fluid samples were collected monthly at the wellheads of the 8 observations wells between February 2005 and March 2008, with baseline data collected between February and April 2005 (Johnson et al., 2011). Following the baseline sampling and start of CO₂ injection, 15 geochemical monitoring events took place between May 2005 and January 2007, followed by an EOR operation switch to a water-alternating gas (WAG) regime in February 2007, with a further 13 monitoring campaigns completed until March 2008 (Johnson et al., 2011).

The δ¹⁸O CO₂ value of injected CO₂ was +28.6 ± 0.2‰ (Johnson et al., 2011). The baseline δ¹⁸O values of the reservoir water at the 8 observation wells varied between −13.5 ± 0.2 and −17.1 ± 0.2‰, dependent upon the impact of a previous water-flood of the reservoir (Table 1). Following initiation of CO₂ injection, reservoir water δ¹⁸O values increased between 1.1 and 3.9‰ at 3 of the 8 observation wells prior to the start of the WAG operation (Fig. 2). This increase was

### Table 1. Summary of oxygen isotope data from CCS storage projects.

| Project | Location | CO₂ source | Total injected CO₂ (tonnes) | Time for change in δ¹⁸O CO₂ | Change in δ¹⁸O water (‰) | References |
|---------|----------|------------|---------------------------|-----------------------------|---------------------------|------------|
| Pembina | Alberta (Canada) | Natural gas processing; refinery; fertiliser plant | 75,000 | 22 months | −17.1 to −13.5 | Johnson et al. (2011) |
| Prague | Czech Republic | Natural gas processing | 1600 | 6 months | +9 | Hovorka et al., (2006), Johnson et al. (2011) |
| Ouyen-Zoet | Australia (USA) | Pure CO₂ production; natural gas processing; refinery | 1000 | 6 months | +0.8 | Johnson et al. (2011) |
| Ketzin | Germany (Germany) | Hydrogen production in coal gasification; oil refining; oxyfuel combustion | 67,271 | 6 months | −19.2 ± 14.5 | Myrttinen et al. (2010), Martens et al. (2012), Emberley et al. (2005) |
| WAG | Saskatchewan (Canada) | Mining; sulphide deposits at Athabasca Oil Sands | 5,000 per day | 3 years, minimum 4 years | +3.8 ± 0.2 | Nowak et al. (2014) |
accompanied by breakthrough of CO2 at these 3 wells, and hence the shifts in $\delta^{18}O$ values of the reservoir water were interpreted to be due to oxygen isotope equilibrium exchange between the injected CO2 and water.

Consequently, the mass of injected CO2 was large enough to influence the oxygen isotope composition of the reservoir water during the Pembina Pilot, and the Johnson et al. (2011) approach presented in Section 2.2 was first used here to estimate CO2 pore-space saturations. Full saturation of the reservoir water with CO2 would only have resulted in an increase of a maximum of 0.4% in the $\delta^{18}O$ values of reservoir water. Similarly, contributions of oxygen from mineral dissolution have been found to represent less than 0.01% of total oxygen.

Johnson et al. (2011) therefore used the oxygen isotope data to quantify CO2 pore-space saturation using Eq. (4), resulting in $S_{CO_2}$ estimates ranging between 12 and 64% for the vicinity of the 3 different observation wells with the largest $\delta^{18}O$ changes in reservoir water. Unfortunately, no data from alternative techniques that could provide comparative CO2 pore-space saturations were published for the Pembina Pilot.

Immediately following the start of the WAG operation in February 2007, reservoir water $\delta^{18}O$ and $\delta^2H$ values showed variable responses for the different observation wells, with increasing, constant or decreasing isotopic values as opposed to values prior to the switch to the WAG regime (Johnson et al., 2011). The differences in oxygen and hydrogen isotope behaviour between the different wells may be due to a variable influence of the injected water isotopic signature on the existing reservoir water isotope regime. In this case, oxygen isotopes may not be suited to quantify CO2 pore-space saturation during WAG operation at an EOR field site.

3.2. Frio

During the Frio-1 experiment at the Frio site located within the South Liberty oil field in east Texas (USA), 1600 t of CO2 were injected during 4–14th October 2004 at 1528–1534 m depth into a 24-m-thick high-permeability sandstone unit of the Oligocene Frio Formation (Hovorka et al., 2006; Kharaka et al., 2006, 2009). The reservoir is characterised by a Na-Ca-Cl type formation water with 93 g/L TDS, and reservoir temperatures and pressures of 60 °C and 150 bar, respectively (Hovorka et al., 2006). As the Frio Formation has a dip of 16° to the south, an observation well was used 30 m updip of the injection well to monitor the target interval. The injected CO2 was refrigerated liquid CO2 trucked to the site, and sourced from a Bay City refinery in Texas and a Donaldsonville fertilizer plant in Louisiana. The injected CO2 for the Frio-1 experiment had a reported oxygen isotope value of $+9‰$ (Kharaka et al., 2006), with no further information about the $\delta^{18}O$ values of the CO2 produced by each of the two sources or their mixing proportions.

CO2 and water samples collected during the Frio-1 experiment using a U-tube system and Kuster downhole sampler (baseline and post-injection geochemical sampling) have provided evidence that the $\delta^{18}O$ value of the reservoir water changed due to interaction with free-phase CO2 (Kharaka et al., 2006) (Table 1). The $\delta^{18}O$ values of the reservoir water shifted from a baseline value of +0.8% to a minimum of $-11.1\%$, with a corresponding increase in the CO2 oxygen isotope composition from $+9\%$ to up to $+43\%$. Kharaka et al. (2006) used the oxygen isotope compositions from the reservoir water and CO2 in mass balance equations to estimate the water to CO2 mass and volume ratios in the reservoir. The oxygen isotope compositions of the water and CO2 from the observation well indicated that initially the system was brine dominated. CO2 pore-space saturation was calculated to be $\sim 10 \pm 3\%$ over the 30 days following CO2 breakthrough at the observation well (Kharaka et al., 2006). Samples collected from the injection well on 4–6th April 2005 yielding the maximum oxygen isotope shift indicated that CO2 filled $\sim 50\%$ of the pore-fluid volume 6 months after the end of injection. Johnson et al. (2011) used their technique and estimated $S_{CO_2}$ values for the Frio-1 experiment for the same time periods, with results of 8% for the first day after CO2 breakthrough and 59% for early April 2005. Consequently, their results are very similar to those of the Kharaka et al. (2006) non-equilibrium oxygen isotope approach.

Downhole pulsed neutron logging showed average CO2 pore-space saturations of $\sim 18.5\%$ on day 4 and $\sim 34\%$ on day 10 (Hovorka et al., 2006). Results from pulsed neutron logging after 6 months indicated that the near-wellbore CO2 pore-space saturation increased to $\sim 50\%$, very similar to the oxygen isotope-based $S_{CO_2}$ estimate (Hovorka et al., 2006). Saturations from arrival times of CO2 and injected tracers (perfluorocarbon tracers, krypton, xenon and sulfur hexafluoride) and using mass balances in a simple radial flow model ranged between 15.6 and 17.1% over the few days following CO2 breakthrough (Freifeld et al., 2005). No tracer method results were reported after the first month following the CO2 injection. Kampman et al. (2014) suggested that due to the dip of the reservoir, the radial flow model probably over-estimates the volume occupied by CO2 and therefore under-estimates the calculated CO2 pore-space saturations. It therefore remains problematic to directly compare the model- and oxygen isotope-based $S_{CO_2}$ estimates. Despite these issues, the comparison of the results based on oxygen isotope data and pulsed neutron logging, for the time period immediately following CO2 breakthrough at the observation well ($10 \pm 3\%$ from oxygen isotopes and 18.5% from pulsed neutron logging) and 6 months later ($\sim 50\%$ for both the geochemical and physical methods), provides evidence that the oxygen isotope approach can be used as a tool to quantify CO2 pore-space saturation.

3.3. Otway

Serno et al. (2016) used oxygen isotope data from samples obtained during the recent CO2CRC Otway Stage 2 B Extension (hereafter referred to as "Otway 2Bext") conducted in October–December 2014 over a time span of 80 days at the CO2CRC Otway Facility in the Otway Basin in southwest Victoria (Australia) to estimate the levels of residual CO2 trapping. The single-well configuration of Otway 2Bext allows fluids to be injected and back-produced through the same well, as opposed to inter-well tests in which fluids are injected in one well and produced through another nearby production or observation well.

During Phase 2 of the field test, 109.8 t of CO2 sourced from the nearby Boggy Creek production well (99.9% purity) and from the Callide A Oxyfuel Project capture plant in central Queensland were injected at 1392–1399 m true vertical depth subsea (TVDSS) into the
Reservoir CO₂ and water samples were collected throughout Phases 1 and 2 using a U-tube system installed in the well (Freifeld et al., 2005). Prior to the drive to residual saturation, baseline δ¹⁸O values of the reservoir water remained constant within a 1σ uncertainty for all sampled baseline samples with a range between −6.3 and −5.6‰ (Serno et al., 2016) (Table 1). Following the initiation of the drive to residual saturation in the reservoir, the water δ¹⁸O values decreased from a baseline value of the fully CO₂-saturated water back-produced from the reservoir, −5.9 ± 0.1‰, to −6.1 ± 0.1‰ within a maximum of 2 days (Fig. 3). Any contribution of oxygen from mineral dissolution was excluded (Serno et al., 2016).

The first 12.2 t of the injected CO₂ that was residually trapped in the reservoir were Callide CO₂ with a δ¹⁸O value of +26.1 ± 0.1‰, while the remaining 97.6 t was Boggy Creek CO₂ with a δ¹⁸O of +29.3 ± 0.2‰. Since no estimates for the mixing of the CO₂ in the reservoir or of variable oxygen isotope signatures of the CO₂ in contact with water in the reservoir were available, Serno et al. (2016) assumed perfect mixing of these two CO₂ sources in the reservoir and derived an average δ¹⁸O of +28.9 ± 0.1‰ based on the amounts of the two injected CO₂ sources. Considering the reservoir water baseline and injected CO₂ δ¹⁸O values, and the reservoir conditions during the field experiment (reservoir pressure varied between 139.3 and 139.5 bar during Phase 2.4, and reservoir temperature between 42.5 and 47.0 °C, with an average ε²H value of 36.8‰), a change up to 2‰ lower δ¹⁸O values of the reservoir water was expected when CO₂-water oxygen isotope equilibrium exchange occurs in the reservoir.

The data from this study were the first to indicate that a change in reservoir water δ¹⁸O values (−0.3 ± 0.2‰) due to oxygen isotope equilibrium exchange between the trapped CO₂ and water occurs over a time span of only a few days. As a result of the field experiment setup, with no structurally trapped CO₂ in the reservoir, Serno et al. (2016) used Eq. (4) to estimate a residual CO₂ saturation of 14 ± 9% for this sample. Although the oxygen isotope shift observed in the reservoir water during Otway 2Bext was relatively small, the oxygen isotope-based result compares well with independent measures from pulsed neutron logging (averaged near-well reservoir saturation of ~8.8%) and of numerical simulation of Kr and Xe tracer injection and recovery data during the field experiment (best estimates between 7.2 and 9.3%) (LaForce et al., 2015), indicating the potential of oxygen isotopes to serve as a geochemical tool to quantify reservoir CO₂ saturation over a time span of only a few days in a single-well configuration test. Furthermore, the choice of a more isotopically distinct injected CO₂ has the potential to improve the accuracy of the isotope-based assessment of residual CO₂ saturation in such field experiments.

### 3.4. Ketzin

During the CO₂SINK project (“CO₂ Storage by Injection into a Natural Saline Aquifer at Ketzin” – subsequently referred to as the “Ketzin project”) at the Ketzin test site near Berlin (Germany), a total of 67,271 t of CO₂ was injected at a depth of ~650 m from 30th June 2008 for 62 months (Martens et al., 2012). CO₂ was injected into the 80 m thick and lithologically heterogeneous Upper Triassic Stuttgart Formation consisting of sandstones and siltstones interbedded with mudstones (Förster et al., 2006). One injection well (Ktzi 201) and 2 observation wells (Ktzi 200 and 202) were used during the field experiment, with Ktzi 201 and 202 being situated 50 and 100 m apart from Ktzi 200, respectively (Myyrinen et al., 2010). Reservoir temperatures and pressures at 650 m depth were ~35 °C and 62 bar, respectively, with a reservoir water TDS of 235 g/L (Myyrinen et al., 2010).
2010; Schilling et al., 2009). The injected CO2 originated from two sources; the primary source was Linde AG food grade CO2 (99.9% purity) that was a by-product of hydrogen production (Martens et al., 2012). Up to the end of September 2011, a total of 51,500 t of the food grade CO2 was injected. The other source was a captured CO2 (99.7% purity) from the oxyfuel pilot plant “Schwarze Pumpe” operated by Vattenfall, of which 1515 t were injected during a trial period from 4th May to 13th June 2011 (Martens et al., 2012).

The injected food grade CO2 had δ18O values ranging between −29.3 and −8.7‰, measured between 30th April and 17th July 2009 (Myrttinen et al., 2010; Novak et al., 2014), with a mean value of −19.2 ± 14.5 (2σ) ‰ (Table 1). Baseline δ18O values of the reservoir water at the injection and observation wells at sampling depths ranging from 625 to 760 m varied between −5.6 and −5.2‰ in June 2008 (Myrttinen et al., 2010). All reported water δ18O values have a 1σ uncertainty of ±0.15‰. Following the start of CO2 injection, the δ18O values of reservoir water at observation well Ktzi 200 remained constant between July 2008 and March 2009 at −5.5 to −5.3‰, except for a sudden drop to −12‰ in December 2008. Similarly, the water δ18O values remained constant at −5.5 to −5.3‰ between August 2008 and March 2009 at observation well Ktzi 202. Although only one reservoir water δ18O value was measured from a depth of 670 m at Ktzi 201 following the start of injection, the sample from December 2008 showed a much lower value of −9.5‰. Myrttinen et al. (2010) suggested that there is a lack of change in the oxygen isotope composition of reservoir waters during the Ketzin project, based on the lack of variability of δ18O values at both observation wells. The lack of significant oxygen isotope shifts in the reservoir water at the observation wells has been interpreted to be due to the mass of injected CO2 being too small to observe a significant shift of oxygen isotope ratios in reservoir waters. Considering the volume of injected CO2, compared to field tests performed at Pembina, Froio or Otway, and since the baseline water and injected CO2 oxygen isotope compositions are distinct enough to change the water oxygen isotope composition at the observation wells as a result of CO2-water interaction considering the oxygen isotope enrichment factor ε18O-H2O of 38.2‰ for a reservoir temperature of 35 °C (Bottinga, 1968), we would expect a change in the reservoir water oxygen isotope composition at the observation wells to lower δ18O values. The lack of water oxygen isotope change at the observation wells may be due to secure storage of large volumes of injected CO2 in pore spaces and through dissolution into reservoir water between the injection and observation wells.

Although only one reservoir water δ18O value was analysed from Ktzi 201 following the start of injection, it is worth comparing the resulting SCO2 estimate from the oxygen isotope shift in this reservoir water sample to independent CO2 pore-space saturation measures. The δ18O value of mean baseline water at Ktzi 201 prior to CO2 injection was −5.6 ± 0.2 (2σ) ‰. Considering the injected δ18OCO2 value of −19.2 ± 14.5 (2σ), fully CO2-saturated reservoir water would have a δ18O-H2O value of −7.6 ± 0.6‰. With a reported δD-H2O value of −9.5 ± 0.2‰ and an oxygen isotope enrichment factor ε18O-H2O of 38.2‰, the fraction of oxygen sourced from CO2 in the reservoir can be estimated as 3.8 ± 1.6‰. Considering the reservoir conditions mentioned above and using Eq. (4), the resulting estimate for S18O2 is 12.8 ± 9.7‰. The large error of the calculated S18O2 is mainly due to the large variability in reported δ18OCO2 values for the injected CO2.

Pulsed neutron logs at Ktzi 201 were run prior to the start of CO2 injection, and again in July 2008 shortly after CO2 breakthrough at Ktzi 200, in June 2009 and in March 2010 (Ivanova et al., 2012). Volumetric CO2 contents based on averaging three pulsed neutron log repeats following initiation of CO2 injection at Ktzi 201 varied between 14 and 19% in the upper part of the target interval (634–642 m depth) and 0–3% in the bottom part (662–664 m depth), with average minimum and maximum values for the interval between 634 and 664 m of 5.5 and 10.0%, respectively (Ivanova et al., 2012). Consequently, our oxygen isotope-based S18O2 value of 12.8 ± 9.7% falls within the range of possible CO2 saturations based on pulsed neutron logging. However, for the Ketzin project, the large range in δ18OCO2 values of injected CO2 results in large S18O uncertainties using the Johnson et al. (2011) approach, limiting its usefulness here.

3.5. Weyburn-Midale

The IEAGHG Weyburn-Midale CO2 Monitoring and Storage project, conducted near the towns of Weyburn and Midale in southern Saskatchewan (Canada), started injecting CO2 into the shallow marine carbonates in the Midale Beds of the Mississippian Charles Formation at ~1500 m depth in September 2000, and will continue injection until approximately 2033 at a rate of ~5000 t/day. The project combines CO2 storage with EOR by injecting CO2 and brine into a depleted oil field (Emberley et al., 2005). From the beginning of the CO2 injection, the injection pattern has been dominated by simultaneous injection of CO2 and water, or WAG injection (Hirsche et al., 2004). Reservoir pressures and temperatures are variable, but average at around 170 bar and 60 °C (Hutcheon et al., 2016). During the project, oxygen isotope data of the injected CO2 and reservoir fluids from observation wells were collected (Johnson et al., 2009; Mayer et al., 2013).

Seventeen fluid and gas sampling surveys were conducted from August 2000 until October 2010, including a baseline sampling survey one month before the start of CO2 injection (Mayer et al., 2013). Approximately 40–55 wells were sampled during each sampling survey, although samples were not always collected from the same wells due to periodic well servicing and production-related shutdowns. Fluid and gas samples were obtained at the wellheads, and δ18O values in CO2 and water and δ2H values in reservoir water were determined as described in Mayer et al. (2013). Analytical uncertainties for gas and water δ18O values are < ± 0.2‰, with an uncertainty of < ± 2.0‰ for water δD values (Mayer et al., 2013). While some of the δ18O data from reservoir waters collected at Weyburn-Midale wells have been presented in Johnson et al. (2009), the majority of the δ18O values for formation waters and all δ18O values for CO2 and δ2H values for formation waters from the Weyburn-Midale project are published here for the first time. Baseline δ18O values of reservoir water collected from the wells varied between −9.8 and −1.2‰, with an average of −6.6 ± 1.8 (1σ) ‰ (Table 1). The injected CO2 was captured after coal gasification in the Dakota Gasification Company’s synthetic plant in Beulah, North Dakota, liquefied by compression and then piped to the Weyburn-Midale oil field (Emberley et al., 2005). The CO2 gas was the first man-made source of CO2 being used for EOR (Kharaika et al., 2013), and had an essentially constant δ18OCO2 value of +3.8 ± 0.2‰.

Although most of the ~40 monitored wells do not indicate an oxygen isotope shift from baseline conditions, repeatedly obtained samples from 5 Weyburn-Midale wells (01–11, 02–12, 05–36, b09–18, d11–12 east) displayed a clear shift to lower oxygen isotope values of reservoir water compared to the respective CO2-saturated reservoir water baseline values (Table 2; Fig. 4). The oxygen isotope shifts of produced water obtained from the different wells are highly variable, with a maximum shift of 9.3‰ in ~8 years at well 01-11 and a minimum shift of 2.4‰ over 8.5 years at well 05-36. Well b09-18 showed an oxygen isotope shift of 8.3‰ from the CO2-saturated baseline value in only 3 years following the start of CO2 injection. The calculated S18O2 values in the vicinity of the sampled wells varied between 5.4 and 35.1‰ (Table 2). These values can be compared to approximations of mean CO2 saturations in the Midale Marly Formation based on time-lapse seismic imaging for four of the monitoring years (Fig. 19 in White, 2013). The approximate values for the locations of the wells indicate rather weak correlations with the oxygen isotope-based CO2 pore-space saturations (Table 2). However, the seismic-based values are only approximated from the maps in Fig. 19 of White (2013), and therefore may be different to the actual value by more than 10%.

Finally, when interpreting changes in CO2 pore-space saturation from the wells in the Weyburn-Midale field, we have to consider that
from the beginning of CO2 injection, the injection pattern was dominated by WAG operation (Hirsche et al., 2004). As observed during the Pembina Pilot (Johnson et al., 2011), this may complicate the interpretation of the oxygen isotope shift in the reservoir water since new sources of water with different oxygen isotope ratios and CO2 saturations are injected that have the potential to disturb the evolving patterns caused by CO2 injection only. Further, injected CO2 was increasingly supplemented by recycled CO2 obtained from producing wells after CO2 breakthrough, potentially resulting in variable injected $\delta^{18}O_{CO_2}$ values. Consequently, it remains uncertain if the oxygen isotope data from the IEA GHG Weyburn-Midale EOR project can be used to quantify CO2 pore-space saturation.

### 3.6. Summary of field project observations

Oxygen isotope data from reservoir water produced during five field projects from around the world provide evidence for isotopic shifts in waters due to oxygen isotope equilibrium exchange with the injected free-phase CO2 in the reservoir. However, oxygen isotope ratios have only been used to quantify CO2 pore-space saturation during three of these five field experiments (Frio, Pembina, and Otway 2Bext). Only one single-well field test (Otway 2Bext) has applied oxygen isotopes as a monitoring tool to quantify CO2 pore-space saturation. The published CO2 pore-space saturation estimates from the Frio, Pembina and Otway 2Bext projects, as well as the measures from the Ketzin pilot study calculated here, are similar to independent measures of CO2 pore-space saturation from the respective field tests, further indicating the viability of using oxygen isotope ratios and the Johnson et al. (2011) approach to quantify CO2 pore-space saturation in cases where the $\delta^{18}O_{CO_2}$ values of the injected CO2 is constant and sufficiently distinct from that of the reservoir water plus $\varepsilon_{CO_2-H_2O}$. The Pembina and Weyburn-Midale EOR projects suggest that the use of this inherent tracer is problematic when aiming to measure CO2 pore-space saturation in a WAG regime due to the injection of new sources of water with different CO2 saturations and oxygen isotope ratios. These new sources of water have the potential to disturb the evolving patterns caused by CO2 injection only. Other than this potential limitation, the studies revealed important issues that can arise during the use of oxygen isotopes to reconstruct reservoir-scale CO2 pore-space saturation and that have to be considered when applying this tool, as outlined in the next section.

### 3.7. Lessons learned about the use of oxygen isotope ratios to quantify CO2 pore-space saturation during field experiments

The oxygen isotope approach of Johnson et al. (2011) has been applied at different CO2 storage sites, proving its validity, but also highlighting a number of issues affecting its effectiveness. The key issues for using this technique are:

1. The approach provides an averaged saturation over the studied vertical interval.
2. The $\delta^{18}O_{CO_2}$ value of the injected CO2 has to be isotopically distinct compared to the $\delta^{18}O$ value of the reservoir water plus $\varepsilon_{CO_2-H_2O}$.
3. The oxygen isotope composition of the injected CO2 and reservoir water should be known, and the $\delta^{18}O$ value of the injected CO2...
should be constant throughout the experiment,
4) Problems arising from the choice of reservoir water sampling tech-
nique and sampling frequency,
5) Differences in field projects with CO2 injection only and WAG op-
eration,
6) Complications in the interpretation of oxygen isotope ratios from
reservoir water in a single-well test versus an inter-well scenario.

The Johnson et al. (2011) approach provides an averaged saturation
over the studied vertical interval, and hence does not take into account
potential small-scale vertical variability in the flows of the CO2 and
water (e.g., Kampman et al., 2014). The vertical resolution of the re-
constructed saturation will depend on the type of sampling, either
sampling at the wellhead, providing an average from the perforated
interval, or using a U-tube or other downhole sampling ports, which
yield more depth-constrained results.

For an oxygen isotope ratio shift in the reservoir water as a result of
CO2-water oxygen isotope equilibrium exchange in the subsurface to be
significantly larger than the analytical uncertainty of δ18O measure-
ments, the δ18O value of the injected CO2 has to be isotopically
distinct compared to the baseline δ18O value of reservoir water plus
εCO2,H2O. This is essential for the application of this technique since a
small distinction similar to the analytical δ18O error results in large
uncertainties in estimated XCO2 and SCO2 values based on Eqs. (3) and
(4). The Frio and Pembina projects revealed relatively large oxygen
isotope shifts in the reservoir water (11.9% for Frio and 1.1-3.9% for
Pembina) as a result of a large difference between the oxygen isotope
ratios of the injected CO2 and the reservoir water plus εCO2,H2O. The
Weyburn-Midale (2.4-9.3% change in δ18O values of the reservoir
water) and Ketzin projects (1.9% change) also displayed a clear oxygen
isotope shift in the reservoir water, however other issues, which are
discussed below, resulted in elevated uncertainties in estimated XCO2
and SCO2 values based on Johnson et al. (2011) from these projects. The
Otway 2Bext project was characterised by a small distinction of the
oxygen isotope ratios of water and CO2, resulting in a very small oxygen
isotope shift in the reservoir water (0.3 ± 0.2‰). Consequently, the
small oxygen isotope distinction resulted in large uncertainties for the
XCO2 and SCO2 estimates from Otway 2Bext.

For the Johnson et al. (2011) method to provide reliable CO2 pore-
space saturation estimates, it is necessary that the baseline δ18O value
of the reservoir water and the δ18O value of the injected CO2 are
accurately known and remain constant throughout the experiment. All
five field projects described above conducted robust monitoring of the
baseline δ18O values in the reservoir water prior to CO2 injection. The
Ketzin, Pembina and Weyburn-Midale projects, with water samples
collected from different monitoring wells, showed different temporal
δ18O shift patterns in the reservoir water obtained from the various
wells.

While the Pembina and Weyburn-Midale projects provided evidence
for essentially constant δ18O values of the injected CO2 throughout
the injection period, the large variation in δ18OCO2 values of CO2 in-
jected from a single source during the Ketzin project (varied between
−29.3 and −8.7‰, Myrtilinen et al., 2010; Nowak et al., 2014) results
in large errors for the assumed injected δ18O value used in Eq. (3)
and in estimated XCO2 and SCO2 values. During the Frio experiment, with
a single injection and observation well, the injected CO2 was sourced
from a refinery and fertiliser plant, but only an average δ18O value of
+9‰ was reported (Kharaka et al., 2006). No further information is
available about the δ18O values of CO2 produced by each of the two
sources or their mixing proportions. This missing information may
introduce large uncertainties in the oxygen isotope composition of the
injected CO2 and its changes throughout the injection period. A solution
to this problem is regular monitoring of the injected δ18O value
throughout the injection period, combined with more complex model-
ling of the CO2 plume movement in the subsurface. CO2 from two dif-
ferent sources was injected during Otway 2Bext, with differences in

their oxygen isotope ratios (+26.1 ± 0.1‰ versus +29.3 ± 0.2‰). Since
no information about mixing of the two CO2 sources in the re-
ervoir was available, Serno et al. (2016) assumed perfect mixing and
calculated a weighted average based on the injected amounts of the two
sources. Considering the small oxygen isotope distinction between the
injected CO2 and reservoir water plus εCO2,H2O during this field test and
the resulting small shifts in reservoir water δ18O values due to CO2-
water oxygen isotope equilibrium exchange, the uncertainty in the
δ18OCO2 value of the injected CO2 results in a significant uncertainty in
the estimated CO2 pore-space saturation. The reservoir water sampling
technique and frequency is another factor that can significantly influence
the reliability of CO2 pore-space saturation estimates. Most CO2 injection
projects were conducted over multiple months or years, with a low frequency of the sampling of re-
ervoir waters. A low-resolution sampling approach potentially results
in the inability to observe small-scale temporal and spatial variability
because the Johnson et al. (2011) approach averages CO2 pore-space
saturation for the reservoir volume described by each sample. Otway
2Bext was the only field project that collected daily reservoir water
samples from the start of CO2 injection and fluid/gas production,
identifying some early breakthrough effects. However, the immediate
fluid sampling during Otway 2Bext may have resulted in the collection
of water samples that had not established full oxygen isotope equili-
brium with the free-phase CO2 in the subsurface, as it can take up to one
week to establish a full equilibrium (Becker et al., 2015; Johnson and
Mayer, 2011).

Both the Frio experiment and Otway 2Bext provided evidence that
the reservoir water sampling technique can have an important influence
on the reliability of the measured water oxygen isotope ratios. Shortly
after the initiation of CO2 injection during the Frio experiment on 4th
October 2004, an oxygen isotope ratio difference of ~41–42‰ was
established between the sampled CO2 and reservoir water (Kharaka
et al., 2006), which remained constant throughout the monitoring
programme (Fig. 5). The reservoir temperature of 60 °C in the Frio
Formation would result in an oxygen isotope enrichment factor of
33.9‰ following Eq. (2), while an oxygen isotope distinction of
41–42‰ indicates temperatures of 16–21 °C. A similar observation has
been made during Otway 2Bext when CO2 samples showed oxygen
isotope ratios that were different to those of the water collected from
the same U-tube sample by a factor that suggests an equilibration
temperature of ~20 °C. Since samples during the Frio experiment were
collected with the same U-tube sampling system used during Otway
2Bext, we suggest that collection of the gas samples at surface may

Fig. 5. Change in the δ18O value of the reservoir water (blue) and injected CO2 (red)
collected with a U-tube system in the observation well during the Frio-1 experiment
(Kharaka et al., 2006), following the period of CO2 injection at 4-14th October 2014
(grey bar). The blue and red dashed lines indicate the baseline δ18O values of reservoir
water and injected CO2, respectively. Shortly after the start of CO2 injection, reservoir
water and CO2 changed their oxygen isotope composition, and a constant δ18O difference
of 41–42‰ between the water and CO2 established. (For interpretation of the references
to color in this figure legend, the reader is referred to the web version of this article.)
cause an isotopic equilibrium reaction at surface temperature, which results in a change in the oxygen isotope signature of the CO₂ gas. The water may also be affected by surface degassing, but the degassing will result in a dominance of water in the system and a very small gas volume, and hence a negligible effect on the oxygen isotope composition of the water. However, this may complicate any approach to quantify CO₂ pore-space saturation using the oxygen isotope compositions of both CO₂ and reservoir water, such as applied by Kharaka et al. (2006). Another potential sampling issue at surface was reported by Serno et al. (2016) who found that there were significant differences in the oxygen isotope composition of waters collected at downhole pressure using the U-tube system during Otway 2Bext, which were completely degassed at surface, and those collected from the production line at surface at atmospheric pressure. This observation has been explained to be the result of incomplete degassing of the water sample collected from the production line, which allows continuous oxygen isotope equilibrium exchange between CO₂ and water in the sampling vessel during storage. Therefore, complete degassing of the collected water samples needs to be assured, either through the use of a downhole sampling device or via collection from a surface production line, followed by complete degassing of the sampled reservoir water.

Two of the five field projects that used oxygen isotope ratios as a monitoring tool were fully (Weyburn-Midale) or partly (Pembina) operated in WAG mode, meaning that water and gas were alternately injected, different to CO₂ injection only. WAG operation may complicate the interpretation of observed oxygen isotope shifts in the reservoir water since new sources of water with different oxygen isotope ratios may be injected that have the potential to disturb the evolving patterns caused by CO₂ injection only. Further, injected CO₂ is normally increasingly supplemented by recycled CO₂ obtained from producing wells after CO₂ breakthrough during WAG operations, potentially resulting in variable injected δ¹⁸O CO₂ values. Immediately following the start of WAG operation during the Pembina Pilot, after a prolonged period of CO₂ injection only, δ¹⁸O and δ²H values of the reservoir water showed variable responses for the different observation wells, with increasing, constant or decreasing isotopic values as opposed to values prior to the switch to the WAG regime (Johnson et al., 2011). The observations from the Pembina Pilot seem to indicate that the interpretation of oxygen isotope data in terms of CO₂ pore-space saturation during field projects with WAG operation may be problematic. The oxygen isotope data from the single-well Otway 2Bext project showed a very similar problem. Isotopic differences between the two water masses that were injected from two different water storage tanks at surface during the drive to residual saturation and that were produced during Phase 2.4 were identified. Fortunately, Serno et al. (2016) were able to use data of methanol injected into the reservoir water and a simple two-endmember mixing model to calculate the fractions of each of the water masses for each reservoir water sample collected during the production phase. This potential issue is specific to a single-well CO₂ injection project where CO₂ and water are co-injected to drive a formation to residual saturation, and can be resolved by frequent reservoir water monitoring.

There are other issues that can be observed during a single-well experiment, as opposed to a field project with an inter-well configuration. During Otway 2Bext, Serno et al. (2016) found higher SCO₂ values further away from the injection well, where the waters thus had a longer reservoir residence time. Although the shifts in the reservoir water δ¹⁸O values compared to baseline conditions for the different days of production during Phase 2.4 remained constant (0.26 ± 0.17‰ for day 1, 0.31 ± 0.15‰ for day 2 and 0.29 ± 0.17‰ for day 3), the reservoir conditions varied from day to day, with increasing reservoir temperatures and resulting decreasing εCO₂-H₂O values (from 36.8% on day 1-36.0% on day 3) and changing parameters A and B, leading to increasing XCO₂ and SCO₂ estimates based on Eqs. (3) and (4). Considering the changes in reservoir temperature over time, the trend in the oxygen isotope shift for the different days of water production during Phase 2.4 may be explained by a higher residual saturation further away from the well, but could also be the result of oxygen isotope exchange with mobile CO₂ from ahead of the region driven to residual, or continuous oxygen isotope exchange between reservoir water and residual CO₂ during its back-production. This clearly complicates the interpretation of the change in reservoir water δ¹⁸O values in terms of CO₂ pore-space or residual saturation during a single-well experiment, but is not crucial for field tests with an inter-well scenario such as the Pembina, Frio, Ketzin and Weyburn-Midale projects.

The oxygen isotope shift in the reservoir water away from baseline values during Otway 2Bext may be simply due to the variable CO₂ volumes the waters were in contact with in the reservoir, with water samples characterised by a longer residence time in the supercritical CO₂-water system from the beginning to end of the production phase. During the back-production, the water may have continued exchanging oxygen with residual CO₂ with variable isotopic signatures in the different regions of the reservoir, resulting in a further perturbation of δ¹⁸O CO₂. It is difficult to resolve the potential contribution of this mechanism with confidence, mainly due to two factors: 1) The residual CO₂ in the different regions of the reservoir may have already been in contact with other waters and had variable oxygen isotope values compared to the initially injected δ¹⁸O CO₂; and 2) it is uncertain if there was enough time for continuous oxygen isotope equilibrium exchange of the reservoir water with the residually trapped CO₂ on its way to the well during back-production. This observation could be crucial if considering using oxygen isotopes to quantify CO₂ pore-space or residual saturation in a field experiment using a single-well configuration. We recommend its influence should be studied further in future laboratory experiments with more isotopically distinct CO₂ and water samples and modelling studies.

4. Applicability of the oxygen isotope method to future CCS projects

Whilst pilot projects tend to use natural CO₂ due to abundance and cost, future integrated CCS projects, by their definition, will use anthropogenic captured CO₂. For the oxygen isotope method to accurately quantify CO₂ pore-space saturation, the δ¹⁸O values of the injected CO₂ and reservoir water have to be isotopically distinct by a value different to εCO₂-H₂O. Therefore, to assess whether the oxygen isotope method will be a useful monitoring tool for real-world, commercial CCS, we review the oxygen isotope ratios of captured CO₂ and compare them to the likely range of δ¹⁸O values of baseline formation waters in storage reservoirs.

4.1. The oxygen isotope ratios of captured CO₂

Industrial processes likely to contribute to CO₂ for geological storage include electricity generation via fuel combustion, gasification processes (e.g. syngas, synfuel and fertiliser production), bioethanol fermentation, steel and cement manufacture, and CO₂ separation processes, applied both to natural gas processing and capture of CO₂. Relevant details of these processes are described by Flude et al. (2016). Sources of oxygen that will contribute to the oxygen isotope ratio of captured CO₂ include: atmospheric oxygen (+23‰; Clark and Fritz, 1997; Kroopnick and Craig, 1972), cryogenically separated oxygen (assumed to be +23‰ but may be higher due to concentration of heavier isotopes in the dense phase during air separation), biomass, limestone (+20 to +30‰; Keith and Weber, 1964), iron ore (+2 to +13‰; Faure, 1986; Nyström et al., 2008), and water and steam. Meteoric waters, excluding regions of extreme climate such as Antarctica, range in δ¹⁸O values from −20 to +10‰ (Clark and Fritz, 1997). Steam is depleted in¹⁸O relative to the residual water, by ~5‰ at 100 °C, and so steam derived from meteoric water will have δ¹⁸O values between −25 and +10‰, depending on the efficiency of
Table 3
Expected oxygen isotope compositions of CO₂ generated by a variety of industrial and energy generating technologies, relative to their source components (feedstock, combustion, atmosphere, etc.) and with likely oxygen isotope fractionations where relevant, as well as observed oxygen isotope compositions in captured CO₂. Subsequent amine capture and physical absorption are not included.

| Process                          | Oxygen sources and δ¹⁸O (in ‰ VSMOW)                  | Modifications to source δ¹⁸O                                      | Hypothetical δ¹⁸OCO₂ (‰ VSMOW) | Reported δ¹⁸O of CO₂ (‰ VSMOW) |
|----------------------------------|------------------------------------------------------|------------------------------------------------------------------|-------------------------------|-------------------------------|
| Natural gas processing CO₂       | CO₂ in equilibrium with groundwater: +10 to +45, depending on temperature and water δ¹⁸O | Possible small (unknown) fractionation during purification      | +5 to +50                     | Ferus Gas Industries +28.6 ± 0.2 Johnson et al. (2011) |
| Natural combustion               | Atmospheric oxygen: − +23                             | Unlikely, but up to −21% for biomass due to diffusive fractionation | +2 to +23                     | PACT combustion flue CO₂ +24 to +29 Flude et al. (2017) |
| Oxyfuel                          | Cryogenic (atmospheric?) oxygen: ≥ +23               | Up tp −21%                                                        | +2 to +23                     | Niederaussem captured CO₂ +19b |
| Gasification/Syngas              | Steam: −25 to +10                                    | Likely small due to high temperatures involved                    | -25 to +17                    | Ferrybridge captured CO₂ +24b |
|                                  | Cryogenic/atmospheric oxygen: ≥ +23                  |                                                                   |                               | Boundary Dam captured CO₂ +18b |
| Fermentation                     | Meteoric water: −20 to +10                            | δ¹⁸O CO₂ − H₂O = −39 to +42% at typical fermentation temperatures | +19 to +52CO₂                 | Calidie A Oxyfuel Project plant, +26.1 ± 0.1 Serno et al. (2016), Flude et al. (2017) |
| Cement                           | Biomass slightly enriched relative to meteoric water  | Unknown                                                          | +21.5 to +26.5                | Linde AG oil refinery −30c |
| Steel industry: ISF              | Atmospheric oxygen: − +23                             | Unknown                                                          |                               | Scotford Upgrader +14 Rock et al., 2014; Shovalier et al., 2014 |
| Steel industry: DRI              | CO from syngas: −50 to +23                           | Unlikely, but up to −21                                           | +2 to +23, most likely ~ +23  | Dakota coal gasification plant +3.8 ± 0.2 Johnson et al., 2009; this study |
|                                  | Iron oxide: +2.3 to +13                               | Unknown                                                          | −24 to +18                    | Bay City refinery and Donaldson fertiliser plant +9 Kharaka et al., 2006 |
|                                  |                                                      |                                                                  |                               | Agrium fertiliser plant +19 Flude et al., 2017 |

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* CO₂ injected at the Ketzin project was a by-product of hydrogen production at the Linde AG oil refinery. The Linde CO₂ was mixed with natural CO₂ prior to injection and published δ¹⁸O values (−29.3 to −8.7‰; Myrttinen et al., 2010; Nowak et al., 2014) represent the mixed CO₂. We estimate the δ¹⁸O value of the refinery component to be −30‰, by correlating published δ¹⁸OCO₂ with δ¹³C CO₂ and extrapolating to the refinery δ¹³C endmember (−30‰ PDB; Nowak et al., 2014).

* Combustion-derived CO₂ was purified using amine capture.

* Combustion-derived CO₂ was purified cryogenically.
The CO₂. The relative influences of isotope fractionation due to combustion and amine capture remain unknown. However, Flude et al. (2017) concluded that the oxygen isotope composition of water involved in amine capture exerts little influence on the resulting δ18O of CO₂ value. This conclusion is corroborated by oxygen isotope data from CO₂ injected during the Pembina project. This CO₂ was captured from waste gas streams separated from (presumably Albertan) natural gas at different Ferus Gas Industries facilities, and had a δ18O value of +28.6 ± 0.2‰ (Johnson et al., 2011) (Table 3). No oxygen isotope data are available for the pre-captured CO₂ co-existing with the natural gas. However, formation waters from oil and gas fields in Alberta have δ18O values between −15 and +1.7‰ (Hitchon and Friedman, 1969), and calculating the δ18O value co-existing with these formation waters gives values between +20 and +35‰ (average of ~ +29‰) (calculation based on temperature and discounting salinity effects). The Pembina CO₂ separated from natural gas thus has an oxygen isotope composition consistent with expected equilibrium conditions in the source reservoirs, and may suggest that oxygen isotope fractionation during amine capture is minimal.

During gasification processes the main source of oxygen is steam, but with up to 50% derived from purified oxygen (Metz et al., 2005). Resulting CO₂ is thus expected to have δ18O values between −25 and +17‰. Gasification-derived CO₂ from a range of refineries and chemical plants has δ18O values between −30 and +19‰ (see Table 3). For the most part these data are consistent with the expected range of δ18O values and small deviations from expected oxygen isotope ratios may be due to changes in the water δ18O value during water purification.

Bioethanol is produced from the feedstock by fermentation of the sugars and starches in the biomass, generating a pure stream of CO₂ (Rossmann et al., 1991). While plant transpiration enriches 18O in plants (and thus their sugars) relative to meteoric water (Monsallier-Bitea et al., 2006), the oxygen contribution from biomass will be minor compared to the volume of added (presumably meteoric) water, which is expected to control δ18O of CO₂ derived from fermentation of biomass with 18O-enriched water. Assuming typical fermentation temperatures of 17–33 °C (Jones and Inglewed, 1994), δ18O of CO₂ will be between +38.6 and +41.8‰, produced capturing CO₂ from fermentation plants with δ18O of CO₂ between +19 and +52‰ (Table 3; Fig. 6).

During cement manufacture, ~50% of the CO₂ is derived from calcination of limestone (Ghoshal and Zeman, 2010; Srivastava et al., 2011), with the remainder due to the energy required to fire the kiln (commonly coal or gas combustion). During decarbonation, 18O is expected to preferentially partition into the CO₂ phase with a CO₂-to-CO₂ enrichment of between +1 and +5‰ (Jolli et al., 2015; Sharp et al., 1996; Shieh and Taylor, 1969). Calculation-derived CO₂ will thus have δ18O of CO₂ values of +21 to +35‰. Assuming a 50:50 mixture of calcination and combination-derived CO₂, CO₂ emitted from cement factories are expected to have δ18O of CO₂ values between +19 and +29‰ (Table 3; Fig. 6), assuming some degree of diffusive oxygen isotope fractionation during combustion.

During steel manufacture, CO₂ is generated from fuel combustion to heat the furnace and from reduction of iron ore (Fe₂O₃, Fe₃O₄) to produce steel via use of reducing agents. Integrated steel plants (ISP) use mostly coal as both fuel and reducing agent (Birat, 2010); combustion is likely to dominate the CO₂ budget resulting in δ18O of CO₂ values of ≤ +23‰. Mini-mill plants use electric furnaces to heat and melt scrap or direct-reduced iron (DRI) (Metz et al., 2005). DRI is produced by reacting iron ore with syngas to form iron, water and CO₂ (Metz et al., 2005). Up to 50% of the oxygen in the resulting CO₂ would be derived from the CO in syngas, (δ18O of −30 to +20‰), with the rest of the oxygen derived from 18O-enriched iron ore oxides giving δ18O of CO₂ values between −14 and +17‰ (Table 3; Fig. 6).
4.2. Oxygen isotope ratios of storage formation waters

Baseline oxygen isotope values for formation waters are available from the Pembina (-17.1 to -13.5‰; Johnson et al., 2011), Frio (+0.8‰; Kharaka et al., 2006), Otway B2ext (-6.3 to -5.6‰; Serno et al., 2006), Ketzin (-5.6 to -5.2‰; Myrkinen et al., 2010), Weyburn-Midale (-9.8 to -1.2‰; Johnson et al., 2009; this study), and CLEAN/Altmark, Germany (-3 to +6‰; Kühn and Münch, 2013) CCS projects. Additional data is available for the Guantao (-10 to -8‰; Pang et al., 2012), and Pontian (-12‰; Varsány et al., 1997) saline aquifers in China and Hungary, respectively. We thus assume an approximate range in δ\(^{18}\)O values of -20 to +10‰ for potential storage formation waters. Assuming a range in storage formation temperatures of 25–120 °C, ε\(_{\text{CO}_2-\text{H}_2\text{O}}\) will range between +40 and +26‰.

4.3. Sensitivity of the oxygen isotope method to baseline conditions and determining the optimal δ\(^{18}\)O value of injected CO\(_2\)

Successful calculation of CO\(_2\) pore-space saturation via the oxygen isotope method requires that the co-existing water and CO\(_2\) have a separation between initial δ\(^{18}\)O values that is different to ε\(_{\text{CO}_2-\text{H}_2\text{O}}\). There will thus be some combinations of initial δ\(^{18}\)O values and reservoir temperatures that this technique cannot be applied to, and a wider range of conditions where precision of the technique will be limited. Here we assess the sensitivity of the technique for two reasons: 1) to facilitate easy identification of the δ\(^{18}\)O values, and thus CO\(_2\) sources, that will be most useful for residual CO\(_2\) saturation field tests; and 2) to assess the likelihood that the oxygen isotope technique can be successfully applied as a monitoring tool to integrated CCS projects, based on the above reviews of δ\(^{18}\)O values, and reservoir water δ\(^{18}\)O values.

An initial assessment of whether the technique can be applied to full scale CCS projects can be made by comparing the “water + ε” field with the anticipated ranges of δ\(^{18}\)O values of captured CO\(_2\) shown in Fig. 6. This shows a high potential for overlap of δ\(^{18}\)O values of ±5‰ for captured CO\(_2\) sourced from most industrial and capture processes and so a more detailed, case-by-case assessment will be required.

The precision and accuracy of CO\(_2\) pore-space saturation estimates based on Eqs. (3) and (4) depends on various parameters, including the δ\(^{18}\)O values of baseline water and CO\(_2\), reservoir conditions (temperature, pressure, salinity), and the CO\(_2\) volume that is trapped in the subsurface. We use a simple modelling approach to calculate the potential error on hypothetical CO\(_2\) pore-space saturations using Eq. (4) for a number of conditions, varying the δ\(^{18}\)O\(_{\text{CO}_2}\) value of the injected CO\(_2\), the δ\(^{18}\)O value of baseline reservoir water, ε\(_{\text{CO}_2-\text{H}_2\text{O}}\), and temperature (or ε\(_{\text{CO}_2-\text{H}_2\text{O}}\)) (Fig. 7). In all models, we assumed a constant analytical error of ±0.2‰ for δ\(^{18}\)O measurements, a reservoir pressure of 150 bar and a reservoir fluid TDS of 0.6 g/L.

Fig. 7 plots the percentage error of the calculated value of CO\(_2\) pore-space saturation against the δ\(^{18}\)O\(_{\text{CO}_2}\) value of the injected CO\(_2\) for different δ\(^{18}\)O values of the initial water, temperature (ε\(_{\text{CO}_2-\text{H}_2\text{O}}\)), and ε\(_{\text{CO}_2-\text{H}_2\text{O}}\). This allows an assessment of the range of δ\(^{18}\)O\(_{\text{CO}_2}\) values for specific reservoir conditions that will allow accurate estimations of S\(_{\text{CO}_2}\), with errors < 10%. For δ\(^{18}\)O\(_{\text{CO}_2}\) - water δ\(^{18}\)O - temperature - ε\(_{\text{CO}_2-\text{H}_2\text{O}}\) combinations that plot above the 10% error threshold, the oxygen isotope method will not provide a reliable estimate of CO\(_2\) pore-space saturation.

An important point highlighted by this model is that, for the most effective use of the Johnson et al. (2011) approach, reservoir conditions must be well known. This includes the reservoir temperature, pressure and fluid TDS, but also the baseline δ\(^{18}\)O range of the reservoir water prior to CO\(_2\) injection.

δ\(^{18}\)O values of injected CO\(_2\) of less than 0‰ are expected to be the most suitable for applying the oxygen isotope method to full scale CCS projects. The relative error in the CO\(_2\) pore-space saturation estimate is primarily controlled by ε\(_{\text{CO}_2-\text{H}_2\text{O}}\). In particular for ε\(_{\text{CO}_2-\text{H}_2\text{O}}\) values of < 20‰, the range of δ\(^{18}\)O\(_{\text{CO}_2}\) values that produce relative errors < 10% for S\(_{\text{CO}_2}\) is rather small. As there are profound differences in reservoir conditions, a comprehensive feasibility study like our simple modelling approach presented in Fig. 7, with additional consideration of the oxygen isotope composition of captured CO\(_2\) (Fig. 6), should be performed in the first stage of each project considering oxygen isotopes as a tool to quantify CO\(_2\) pore-space saturation in a storage reservoir.

5. Conclusions

CO\(_2\) pore-space saturation is a parameter that has been difficult to assess using previous geophysical and geochemical monitoring techniques, but one which is crucial for determining the efficiency of a CO\(_2\)
storage site. Our review of studies from CO2 storage projects around the world illustrates that the oxygen isotope composition of reservoir water changes due to oxygen isotope equilibrium exchange with CO2 when large amounts of free-phase CO2 are in contact with the water in the formation. Field experiments at EOR sites in Texas and Alberta show that oxygen isotope shifts in reservoir waters from baseline conditions due to CO2-water oxygen isotope equilibrium exchange can be used to estimate CO2 pore-space saturation using a multi-field configuration (Johnson et al., 2011; Kharaka et al., 2006). Oxygen isotope data from the Otway test facility in Australia were the first from a field project with a single-well configuration that have indicated the potential of using oxygen isotopes to quantify residual trapping levels of CO2 in a reservoir over a time span of only a few days (Serno et al., 2016).

Hence, we find that these field, laboratory and theoretical studies provide evidence for the viability of using oxygen isotopes and the Johnson et al. (2011) model to quantify CO2 pore-space saturation on a reservoir scale during field experiments with either a multi- or single-well configuration. These field tests clearly indicate that it is essential to fully understand the baseline reservoir conditions and oxygen isotope compositions of the reservoir water and injected CO2 prior to the initiation of injection. This baseline information is necessary to predict the extent of the expected δ18O shift in reservoir water. It is also required to estimate the time it takes for reservoir water and CO2 to achieve full oxygen isotope equilibrium in the formation, which can be up to one week (Becker et al., 2015; Johnson and Mayer, 2011).

We find that a large isotopic distinction of the injected CO2 and reservoir water (or injected water in case of a single-well CO2 injection test), considering the temperature-dependent CO2-water oxygen isotope enrichment factor, is crucial for the development of oxygen isotope shifts in the reservoir water significantly larger than the analytical uncertainty of measured δ18O values. The use of a single CO2 source with a well-defined oxygen isotope signature would avoid uncertainties in the injected δ18O CO2.

CO2 produced using the various carbon capture technologies can serve as a relatively inexpensive gas source for small or large-scale injection into storage reservoirs (and will ultimately be injected for geological storage). A comprehensive review of the limited data available from captured CO2 as well as hypothetical considerations of oxygen isotope ranges for the different techniques, indicates that it is currently difficult to specify precise oxygen isotope ranges for the different captured CO2 sources. Consequently, potential CO2 sources for storage projects should be analysed prior to injection to assess if oxygen isotopes can be applied as a reliable inherent tracer.

Although oxygen isotopes can provide a simple and inexpensive monitoring technique to quantify small and large-scale CO2 pore-space or residual CO2 saturation changes near and further away from a well, it has its known limitations and will not be applicable in all cases. Therefore, a combined geophysical and geochemical monitoring programme would be most effective in determining the fate of the injected CO2 in a storage reservoir and would provide a commercial operator with greater reassurance of the viability of their proposed storage site in terms of structural and residual CO2 trapping levels.

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