

Review

Assessing the usefulness of the isotopic composition of CO₂ for leakage monitoring at CO₂ storage sites: A reviewB. Mayer^{a,b,*}, P. Humez^a, V. Becker^a, C. Dalkhaa^a, L. Rock^c, A. Myrntinen^d, J.A.C. Barth^d^a Department of Geoscience, 2500 University Drive NW, University of Calgary, Calgary, Alberta, Canada T2N 1N4^b Carbon Management Canada Inc., 3535 Research Road NW, Calgary, Alberta, Canada T2L 2K8^c Shell Canada Limited, 400, 4th Avenue SW, Calgary, Alberta, Canada T2P 2H5^d GeoZentrum Nordbayern, Department of Geography and Geosciences, Friedrich-Alexander Universität Erlangen-Nürnberg, Schlossgarten 5, 91056 Erlangen, Germany

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ABSTRACT

Geological storage of injected CO₂ is a promising technology to reduce CO₂ emissions into the atmosphere. Tracer methods are an essential tool to monitor CO₂ plume distribution in the target formation and to enable tracking potential leakage of CO₂ outside the storage reservoir. Here, we demonstrate that the isotopic composition of CO₂ can serve as a suitable tracer at large CO₂ injection sites provided that the injected CO₂ is isotopically distinct from background CO₂ sources that are usually composed of dissolved inorganic carbon, bedrock-derived carbon, and soil CO₂. Very favourable conditions for this tracer approach exist if δ¹³C values of injected CO₂ are more than 10‰ different from those of baseline CO₂ and other dissolved inorganic carbon species at the CCS site. In this case, changes in δ¹³C values accompanied with increasing concentrations of CO₂ or DIC in samples obtained regularly at monitoring sites within or above the storage reservoir indicate arrival of injected CO₂. The proportion of injected CO₂ contributing to the obtained samples can be quantified when carbon isotope fractionation effects are either negligible or thoroughly known. We point out several areas where additional detailed information on carbon isotope effects during phase change, transport and geochemical reactions is desirable to refine this tracer approach for temperature, pressure and salinity conditions relevant for CO₂ storage sites. Oxygen isotope ratios of injected CO₂ were not found to be a conservative tracer due to oxygen isotope exchange between CO₂ and water on time scales of hours to a few days. δ¹⁸O measurements on CO₂ and H₂O have, however, revealed pore space saturation with CO₂ and hence indicate the presence of injected CO₂ within CO₂ storage reservoirs. We suggest that the stable isotopic composition of injected CO₂ is a suitable tracer for assessing the movement and fate of injected CO₂ in the target reservoir and for leakage detection at CO₂ storage sites, provided that the injected CO₂ is isotopically distinct from background CO₂ sources. A key advantage is that this tracer approach does not depend on the co-injection of additional tracers and hence can be continuously used in large-scale commercial storage projects with CO₂ injection rates exceeding 1 million tonnes per year at reasonable cost.

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1. Introduction

Carbon capture and geological storage (CCS) is a promising technology for reducing CO₂ emissions into the atmosphere from fossil fuel intensive industries (IPCC, 2005). An increasing number of pilot sites have been established over the last few years and a number of CCS projects with injection rates exceeding 1 million tonnes (Mt) of CO₂ per year have been established or are in the planning phase (<http://www.iea.org/etp/tracking/ccs/index.html>). For instance, in 2015, CO₂ injection will start at the Quest CCS Project in Alberta, Canada. Here, the CO₂ is captured from the Scotford oil sands bitumen upgrader located northeast of Edmonton (Alberta, Canada). Up to 1 Mt of CO₂ per year will be injected into the Basal Cambrian Sandstone, a saline aquifer located at a depth of about 2 km below ground surface.

For these CO₂ injection sites, existing or emerging regulations will likely require monitoring of CO₂ plume distribution within the target reservoir. In addition, monitoring above the storage reservoir may be required to assess whether CO₂ leakage occurs. Various monitoring approaches have been employed at CO₂ storage sites worldwide to track the movement and the fate of injected CO₂ including geophysical (seismic, geoelectric, electromagnetic techniques), geochemical, and satellite-based approaches (InSAR etc.) among others. For instance, at the 1 Mt CO₂/year scale Sleipner project in Norway, time-lapse seismic monitoring techniques have been used (Chadwick et al., 2006). At the In Salah CO₂ project in Algeria (1 Mt CO₂/year), 3D and 4D seismic surveys, geochemical approaches, and satellite-based technologies have been deployed to monitor the CO₂ in the reservoir (Mathieson et al., 2011; Shi et al., 2012). There have also been a number of smaller CO₂ pilot injection studies conducted such as the Pembina Cardium project in Alberta (Canada) with 75,000 tonnes of CO₂ injected between 2005 and 2008 (Hitchon, 2009; Johnson et al., 2011b), the Otway project in Victoria (Australia) with 65,500 tonnes of CO₂ over 17 months (Boreham et al., 2011), the German Ketzin project with 60,000 tonnes of CO₂ between 2008 and 2012 (Martens et al., 2012) and the Frio Brine Pilot project in Texas (USA) with 1600 tonnes of CO₂ injected over 10 days (Hovorka et al., 2006; Hovorka and Knox, 2003). In all these projects, some geophysical, geochemical and/or other monitoring approaches have been employed to trace the fate of injected CO₂ in a variety of geological and hydrogeological settings. Knowledge gained during these field experiments revealed that seismic techniques are suitable to identify large CO₂ plumes in sufficiently thick injection reservoirs, but that quantification of CO₂ saturation in the storage reservoir is difficult especially at

$0.2 < S_{\text{CO}_2} < 0.7$ (S_{CO_2} = pore space saturation with CO₂). Electrical resistivity tomography (ERT) has been shown to be more efficient in determining pore space saturation with injected CO₂, but requires pre-installation of detectors in selected monitoring wells and hence is restricted to the vicinity of these pre-selected wells. Satellite-based techniques have also been demonstrated to be effective in identifying ground heave above major CO₂ plumes provided that the surface coverage is suitable for this technique. However, none of these techniques are efficient in tracing reactions of injected CO₂ (such as dissolution in formation waters) or the movement of small amounts of injected CO₂ at fringes of the CO₂ plume within the injection reservoir. Nor is leakage of small amounts of CO₂ outside of the storage reservoir detectable with these techniques.

Geochemical techniques for tracing the movement, fate and reactions of injected CO₂ are based on the ability to obtain fluid and gas samples from observation wells either with down-hole tools (e.g. u-tubes), at the wellhead, or via the use of down-hole sensors for in situ measurements where possible. A key pre-requisite for this approach is the thorough determination of baseline conditions, such as pH values, alkalinity, concentrations of major and minor cations, anions and trace elements, and stable isotope ratios of water and selected dissolved constituents in formation waters prior to CO₂ injection. Furthermore, the baseline composition of gases including CO₂ in the reservoir and overlying formations needs to be determined and characterization of noble gas distributions (He, Ne, Ar, Kr, Xe) may be an additional asset (Gilfillan et al., 2009). The radioactive isotope ¹⁴C may serve as an effective additional tracer for distinguishing CO₂ injected into storage reservoirs from baseline CO₂ especially in near-surface environments. For instance, during potential CO₂ leakage, ¹⁴C-free fossil fuel-derived CO₂ can be readily distinguished from ¹⁴C-containing CO₂ derived from the biosphere and pedosphere (Klusman, 2011; Romanak et al., 2013).

After commencement of CO₂ injection, continued geochemical monitoring often reveals changes in gas and fluid compositions from which the physical movement of injected CO₂ and reactions of CO₂ with formation waters and reservoir rocks can be determined provided that a sufficient number of observation wells are accessible in and above the reservoir for water and gas sampling. A further option is to co-inject artificial tracers with the CO₂ stream to determine the movement of the injected gas.

The usefulness of artificial tracers co-injected with CO₂ has been demonstrated in several CCS projects. Ideally, such tracer compounds should occur in low concentration in the environment, be resistant to degradation and retardation, environmentally safe, and

should undergo similar mass transfer processes as CO₂. In the In Salah project, perfluorocarbon tracers (PFTs) were added to the CO₂ streams at individual injection wells to assist with the determination of the CO₂ breakthrough at an observation well (KB-5) in the natural gas field (Ringrose et al., 2009). In the Ketzin project in Germany, krypton and SF₆ were used for verification of the arrival of injected CO₂ at observation wells (Martens et al., 2012). In the Otway project per-deuterated methane (C²H₄), sulfur hexafluoride (SF₆) and krypton (Kr) were used as additional tracers, which were successfully added down-hole after 1000 tonnes of gas were injected (Stalker et al., 2009). Similarly at the Frio Brine Pilot, PFTs, SF₆, C²H₄, and Kr were all deployed to aid in the tracing of the movement of the injected CO₂ (Hovorka et al., 2006). Also, krypton, xenon, PFTs and SF₆ were used at the South East Regional Carbon Sequestration Partnership carbon storage project at Cranfield (MS, USA) as reported by Hovorka et al. (2011). These conservative artificial tracer compounds have proven highly effective in tracing direction and speed of movement of the injected gas in the reservoir at small-scale CO₂ injection pilots. However, due to their different diffusion coefficients, densities, and potential reactivities (Myers et al., 2014; Stalker et al., 2015), their suitability to provide information about geochemical reactions of the injected CO₂ in the subsurface may be limited. Furthermore, co-injection of sufficient amounts of artificial tracers at CO₂ storage sites with injection volumes of the order of 1 Mt of CO₂ per year is very costly (Watson and Sullivan, 2012) and may be cost-prohibitive.

An alternate approach is to use the stable isotope composition of injected CO₂ as a cost-effective inherent tracer for the movement and the fate of injected CO₂. This is particularly effective in cases where the isotopic composition of injected CO₂ is different from those of related aqueous and gaseous CO₂ compounds at the CO₂ storage site at baseline conditions. This approach has been tested with considerable success for tracing the movement and the fate of injected CO₂ in mature oil fields, saline aquifers and at natural analogue sites (Assayag et al., 2009a; Johnson et al., 2011b; Kharaka et al., 2006a; Leuning et al., 2008; Mayer et al., 2013; Myrntinen et al., 2010b). Carbon (C) isotope ratios of CO₂ have been used to track the movement of injected CO₂ in mature oil fields and saline aquifers and the extent of solubility, ionic, and mineral trapping of injected CO₂ (Emberley et al., 2005; Raistrick et al., 2006). In addition, the oxygen (O) isotope ratios of CO₂ and reservoir water have been used to estimate pore space saturation with CO₂ in injection reservoirs (e.g. Johnson et al., 2011a,b; Kharaka et al., 2006b). To apply this approach effectively, it is essential to characterize the isotopic composition of baseline C compounds in formation water in the reservoir and in overlying formations, shallow aquifers, and in the soil zone. Another pre-requisite is that isotope fractionation effects (i.e. changes in isotope ratios due to phase change, (bio-)geochemical reactions or reactive transport) occurring during movement and reaction of injected CO₂ in the subsurface are either negligible or known at all relevant pressure (*p*), temperature (*T*) and salinity (*s*) conditions.

Under these circumstances, isotopic methods in conjunction with geochemical approaches may allow a rapid and accurate assessment of the fate of CO₂ both within the injection reservoir and during potential CO₂ leakage from the host-reservoir into overlying formations at moderate costs, and without the need to introduce artificial compounds. The purpose of this review paper is to assess under which conditions the stable isotope composition of injected CO₂ can serve as an effective tracer for the movement and fate of CO₂ not only in the injection reservoir but also during potential leakage from the storage reservoir. This was accomplished by a comprehensive review of known C and O isotope effects that may affect CO₂ and other C compounds under conditions relevant to CCS settings. We also identify knowledge gaps regarding C and O isotope effects that may affect CO₂ in CCS settings and recommend

approaches to close these knowledge gaps. This will enhance the understanding under which circumstances the isotopic composition of CO₂ can serve as a suitable tracer for movement and in-reservoir processes affecting injected CO₂. This knowledge is also valuable for assessing potential leakage of CO₂ from storage reservoirs into overlying formations, shallow aquifers and soils, and for addressing false leakage claims.

2. Scenarios and processes considered

To assess under which conditions the stable isotope composition of injected CO₂ can serve as an effective tracer for the movement and fate of CO₂ within and outside of the injection reservoir, it is necessary to identify the most likely leakage scenarios together with the most relevant processes affecting the isotopic composition of CO₂. Here, we consider the injection of supercritical CO₂ either into a saline aquifer or into a mature oil or gas field with a considerable amount of formation water present in the reservoir. At an injection rate of about 1 million tonnes of supercritical CO₂ per year and depths between 1 and 3 km, we estimate based on TOUGHREACT (Xu et al., 2011) modelling of a 40 m thick sandstone reservoir with 18% porosity and 100 mD permeability that the top of the CO₂ plume would migrate circa 5 km laterally after 25 years of injection, while the CO₂ accumulates below a tight and effective caprock as shown in Fig. 1.

In case that CO₂ leaks out of the storage reservoir, the most likely scenarios include point leakages along imperfectly sealed wellbores penetrating the caprock. These might be injection wells, monitoring wells, or previously completed offset wells (Fig. 1). Leakage through the caprock (Celia and Nordbotten, 2009) is less likely when thorough site selection criteria have been applied that verified sufficient caprock integrity. In either case, isotopic and geochemical leakage monitoring strategies should include systematic sampling of gases and liquids from formations overlying the storage reservoir to detect potential impacts of leaking CO₂ that migrates upwards from the reservoir. In addition, shallow aquifers, soil gases, and the near-surface atmosphere should be monitored at CO₂ storage sites to verify that no impact from the injected CO₂ is observed (de Caritat et al., 2009; Klusman, 2011; Leuning et al., 2008).

For tracing the movement and fate of injected CO₂, the isotopic composition of injected CO₂ must be sufficiently different from that of C-containing compounds (CO₂, HCO₃[−], etc.) at the storage site. In addition, potential changes of isotope ratios: (a) due to phase changes of CO₂ (e.g. from supercritical to subcritical CO₂), (b) during transport processes in gaseous, liquid or supercritical phases in and above the reservoir, and (c) associated with geochemical reactions induced by the presence of injected CO₂, should either be negligible or thoroughly known.

2.1. Phase changes of CO₂

At temperatures and pressures above the critical point (31.4 °C and 7.39 MPa), CO₂ occurs in supercritical state (CO_{2sc}). Storage reservoirs usually are sufficiently deep to allow injected CO₂ to remain in this phase (CO_{2sc}) while some CO₂ will dissolve in the saline formation water (Duan and Sun, 2003). In case of leakage, the buoyant CO₂ may migrate upwards through geological strata with lower pressures and temperatures resulting in gaseous CO₂. Hence, the phase change of CO₂ from supercritical to subcritical is mostly relevant for the monitoring of potential leakage scenarios, when CO_{2sc} reaches overlying strata at lower pressures and temperatures. The phase change from super-critical to sub-critical conditions for CO₂ will occur usually at depths between 750 and 800 m assuming a typical geothermal and hydrostatic gradient of 3 °C/100 m

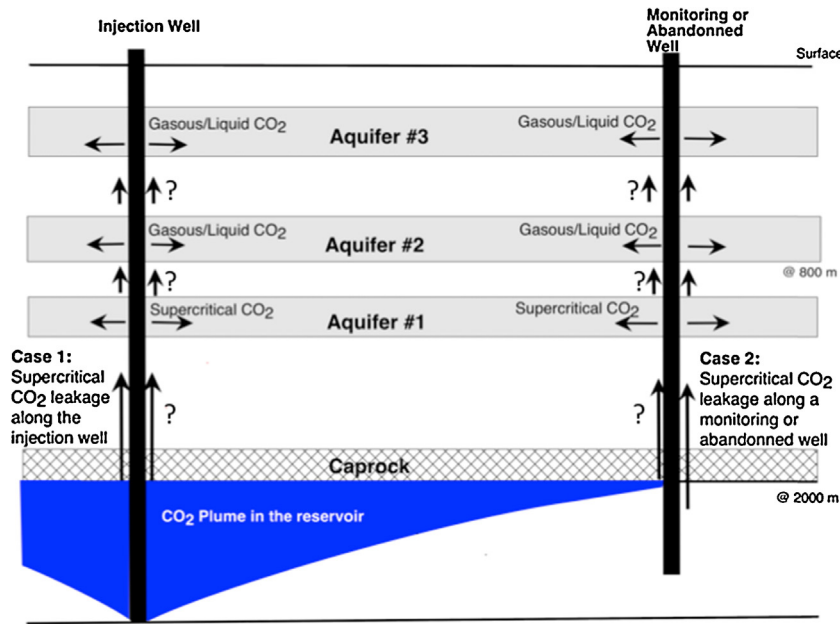


Fig. 1. Conceptual model of potential leakage scenarios predominantly assumed to occur along imperfectly sealed injection wells, observation wells, or abandoned wells.

and 0.01 MPa/m, and a surface temperature of 10 °C (Spycher et al., 2003).

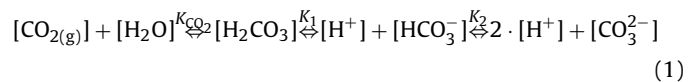
2.2. Transport mechanisms

Geological formations targeted for CO₂ injection are usually porous media initially occupied by in situ fluids such as saline waters, hydrocarbons or both. The injection of supercritical CO₂ increases the pressure in the formation near the injection well and permits the CO₂ to enter the pore space of the target formation while displacing in situ formation fluids via advective transport. Upwards migration of buoyant fluids with lower density compared to surrounding phases is also a form of advective flow. Diffusional transport is the movement of particles induced by concentration gradients. Advective and diffusive processes may happen simultaneously at CO₂ storage sites. Diffusion-dominated transport occurs when advective flow is low or non-existent. This is the case in units with low permeability such as caprocks, and also in environments where differences in pressure heads are low. The latter is for instance the case when CO₂ dissolves into stagnant or slow moving formation water or during CO₂ migration into shallower formations while leakage rates are small. Additional factors that influence CO_{2sc} movement in the subsurface include the lower viscosity of CO_{2sc} compared to saline formation water. Consequently, CO₂ may migrate faster than the in situ formation fluids (Celia et al., 2005; Nordbotten et al., 2005). Furthermore, the presence of several different phases such as supercritical CO₂ and saline water may decrease the permeability of the target formation and slow down CO_{2sc} migration (IPCC, 2005). During the latter, capillary forces retain some CO₂ in the pore space, a process commonly referred to as residual CO₂ trapping.

2.3. Geochemical reactions

Injection of CO₂ triggers a variety of geochemical reactions in storage reservoirs as well as in overlying aquifers in the case of CO₂ leaking out of the reservoir. Primarily, CO₂ will dissolve into formation water. The rate of dissolution depends on temperature, pressure and salinity. Generally, the solubility of CO₂ in water increases with pressure, and decreases with temperature

and salinity (Stumm and Morgan, 1996). CO₂ dissolution also controls the equilibrium with carbonate minerals in the subsurface via formation of carbonic acid (H₂CO₃) followed by dissociation into bicarbonate (HCO₃[−]) and protons (H⁺) resulting in a decrease of pH values (Eq. (1)). This process is often referred to as solubility trapping of injected CO₂:

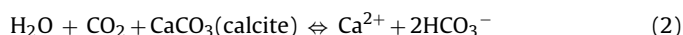


The distribution of dissolved inorganic carbon (DIC) species depends on pH and can be calculated for both open (P_{CO_2} is constant) and closed system conditions (total inorganic C is constant) with respect to CO₂. In low salinity groundwater at near-atmospheric pressures, dissolved CO_{2(aq)} and H₂CO₃ are the dominant DIC species at pH values below 4.3, the sum of CO_{2(aq)} and H₂CO₃ are often expressed as H₂CO₃^{*}. Duan and Sun (2003) presented an approach to derive CO₂ solubilities in pure H₂O and aqueous NaCl solutions in the temperature range from 0 to 260 °C and pressures up to 200 MPa. Duan et al. (2006) extended this model to Na⁺, K⁺, Ca²⁺, Mg²⁺, Cl[−] and SO₄^{2−} containing solutions up to a molality of 4.5, making it applicable to many CCS settings.

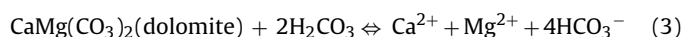
Between pH values of 6.4 and 10.3, HCO₃[−] dominates DIC, whereas above a pH of 10.3, CO₃^{2−} is predominant in low salinity groundwater at near-atmospheric pressures (Clark and Fritz, 1997). Speciation of DIC is affected by high salinities as well as high pressures and temperatures (Becker et al., 2011). Li and Duan (2007) developed a model that combines the prediction of CO₂ solubility, activities, dissociation constants and pH in the CO₂–H₂O–NaCl system for 0–5 M solutions up to 250 °C and 100 MPa using Pitzer's approach to calculate activity coefficients (Pitzer and Mayorga, 1973). This approach allows to predict the pH dependence of the DIC speciation at reservoir conditions, which is essential to accurately predict the distribution of H₂CO₃, HCO₃[−] and CO₃^{2−} and the associated carbon isotope fractionation between DIC and CO_{2(g/sc)}.

As a consequence of the dissolution of injected CO₂ and the formation of H₂CO₃^{*}, the pH value of the formation water will decrease and often changes the initial water–rock equilibrium. This has been

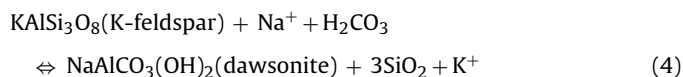
demonstrated by measurements of fluids obtained in the vicinity of injection and observation wells at selected CCS sites or by geochemical modelling (André et al., 2007; Audigane et al., 2007; Gaus, 2010; Gunter et al., 1997; Lagneau et al., 2005; Xu et al., 2004). Geochemical reactions have also been studied in the context of potential impacts of leaking CO₂ into freshwater aquifers and were recently summarized in an IEA report and selected review papers (IEA GHG, 2011; Lemieux, 2011; Lions et al., 2014a), and in various site-specific studies (Apps et al., 2009, 2010; Humez et al., 2013, 2014; Keating et al., 2013; Trautz et al., 2013; Viswanathan et al., 2012; Wilkin and DiGiulio, 2010). Depending on the reservoir or aquifer type, both carbonate and siliciclastic minerals may be involved in dissolution reactions (Eqs. (2)–(4)). Particularly carbonates have a strong buffering effect on the pH value in the formation water (Johnson et al., 2009; Kharaka et al., 2006a, 2009). In carbonate-containing formations, the predominant congruent dissolution reactions include (Gunter et al., 1993):



or



In siliciclastic formations, carbonic acid may facilitate hydrolysis and dissolution of silicate minerals such as feldspars thereby resulting in increasing pH values of formation water (Matter and Kelemen, 2009), while the CO₂ consumed may precipitate as a solid carbonate mineral (Eq. (4)). This process is commonly referred to as mineral trapping (Bachu et al., 1994; Gunter et al., 2004). An example for such reaction is the formation of dawsonite:



Dissolution equilibria between aqueous fluids and primary minerals cannot always be attained, especially in systems where low temperatures lead to slow rates of chemical reactions. While dissolution of CO₂ into formation fluids is expected to be rapid, the rate at which dissolved CO₂ reacts with primary minerals and the rates at which secondary minerals precipitate are much slower (Gunter et al., 1997) and hence reaction kinetics must be considered.

3. Stable isotope fundamentals

Several excellent resources provide detailed information on the application of stable isotope techniques (e.g. Clark and Fritz, 1997; Mook, 2000). Here, a brief overview of stable isotope fundamentals that are relevant for tracing injected CO₂ is provided. Carbon has two stable isotopes, ¹²C and ¹³C with average natural abundances of 98.93% and 1.07%, and oxygen has three stable isotopes, ¹⁶O (99.757%), ¹⁷O (0.038%), and ¹⁸O (0.205%) (Berglund and Wieser, 2011). In nature, considerable variations in the ratios of the two most abundant C (¹³C/¹²C) and O (¹⁸O/¹⁶O) isotope ratios are observed. These can be used for tracing sources and reactions of CO₂ in surface and subsurface environments. Variations of stable isotope ratios are usually expressed in the δ (delta) notation (Eq. (5) for stable C isotopes) in per mil (‰) deviation from an internationally accepted standard.

$$\delta^{13}\text{C} = \left(\frac{(^{13}\text{C}/^{12}\text{C})_{\text{Sample}}}{(^{13}\text{C}/^{12}\text{C})_{\text{Std}}} - 1 \right) \times 1000 [\text{‰}] \quad (5)$$

Isotope fractionation is caused by slightly different equilibrium constants for the different isotopes involved in a specific physico-chemical reaction and may cause significant changes in δ¹³C and δ¹⁸O values of CO₂ or other C-containing compounds.

These changes in stable isotope ratios are commonly denoted by the isotope fractionation factor α, which is defined as

$$\alpha_{\text{X-Y}} = \frac{\delta_{\text{X}} + 10^3}{\delta_{\text{Y}} + 10^3} \quad (6)$$

for the phases or compounds X and Y between which isotope fractionation occurs. The extent of isotope fractionation between two phases or compounds is often reported as 10³ ln α, approximating the isotopic difference ε (also called the isotope enrichment factor) between the δ values of two reacting compounds in ‰. If the isotope fractionation factor α for a chemical reaction is known, changes in δ¹³C or δ¹⁸O values of the substrate or the product can help to identify and quantify these processes under equilibrium as well as non-equilibrium (e.g. kinetic) conditions.

Kinetic (or non-equilibrium) isotope effects occur during unidirectional processes (e.g. chemical reactions, evaporation, metabolic effects, or diffusion). During diffusion the mobility of the molecule containing the heavy isotope is decreased, which leads to a smaller diffusion coefficient. Consequently, the δ value of the product or diffusing compound is typically lower than that of the substrate.

The partitioning of stable isotopes between two reservoirs where one reservoir progressively decreases in size is described by a Rayleigh-type equation (e.g. Clark and Fritz, 1997). For instance, if the light isotope is preferentially allocated into the product of the reaction, the heavy isotope progressively accumulates in the reactant. A logical consequence is that the product will eventually assume the δ value of the substrate as the reaction progresses towards completion (e.g. no reactant left). A more detailed description of the Rayleigh equation as it applies to stable isotope partitioning is provided by Kendall and Caldwell (1998).

4. Stable isotopes as a tracer for injected CO₂

4.1. Typical baseline isotopic compositions

The δ¹³C values of baseline DIC species in formation waters and groundwater depend on the C isotope ratios of the predominant C source (including potentially free phase CO₂ in gaseous or supercritical state) modified by equilibrium isotope fractionation between the predominant DIC species dependent on pH (Clark and Fritz, 1997). Table 1 summarizes baseline δ¹³C values for CO₂ and DIC at selected CO₂ injection sites and pilot projects. Baseline δ¹³C values for CO₂ typically range from −24 to −16‰ indicating that a large proportion of CO₂ is derived from organic carbon sources. Baseline δ¹³C values for DIC prior to injection of CO₂ varied between −22 and 0‰. This wide range suggests that C is derived from a variety of sources and is additionally affected by associated isotope effects during DIC conversions and other reactions such as outgassing of CO₂.

Organic C in soils, sedimentary rocks and crude oils typically has δ¹³C values of −26 ± 8‰ and CO₂ derived from this source has similar C isotope ratios. During CO₂ dissolution, ¹²C accumulates with slight preference over ¹³C (Vogel et al., 1970), resulting in a δ¹³C value of CO_{2(aq)} that is circa 1‰ lower than that of the source CO₂ (on average −27‰). Subsequent hydration of CO_{2(aq)} favours ¹³C (Mook et al., 1974), and hence HCO₃[−] will have a δ¹³C value that is, depending on temperature, between 4 and 10‰ higher (e.g. −22 to −16‰) than that of the source CO₂. In addition to CO₂ dissolution and dissociation of H₂CO₃, water–rock interactions can also influence δ¹³C values of DIC. Reservoir rocks composed of primary marine carbonates are characterized by δ¹³C values of +2 ± 4‰ (Veizer et al., 1999). If H₂CO₃ derived from soil CO₂ dissolves primary carbonates, e.g. in shallow aquifers, the resulting δ¹³C values of HCO₃[−] typically vary from −16 to −5‰ (e.g. Appelo and Postma, 2005; Deines et al., 1974; Kloppmann et al., 1998;

Table 1
Measured $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values of baseline compounds and injected CO_2 at various CO_2 injection and storage sites.

CCS project	Formation and CO_2 injection	End-members		Injected CO_2			
		Baseline					
		$\delta^{13}\text{C}_{\text{CO}_2}$ [‰]	$\delta^{13}\text{C}_{\text{DIC}}$ [‰]	$\delta^{18}\text{C}_{\text{H}_2\text{O}}$ [‰]	$\delta^{18}\text{O}_{\text{CaCO}_3}$ [‰]	$\delta^{13}\text{C}$ [‰]	$\delta^{18}\text{O}$ [‰]
Pembina Cadium (Alberta, Canada) Johnson et al. (2011a,b)	EOR operation Siliclastic reservoir 1650 m depth	–15.9 to –23.5	n.d.	–13.5 to –17.1	–4.6 to –16.8	–4.7	+28.6
Weyburn (Saskatchewan, Canada) Johnson and Mayer (2011)	75,000 tonnes of CO_2 injected Carbonate reservoir 1500 m depth	–12.7 on average	–1.8 on average	n.d.	n.d.	–20.4	n.d.
Mayer et al. (2013)	20 × 10 ⁶ tonnes of CO_2 injected Dolerite-containing aquifer 250 m depth	n.d.	–17.8	–8.6	–14 to –6	–51.1 ^a	+2.1 ^a
Lamont-Doherty Earth Observatory test site (USA) Assayag et al. (2009b)	1300 L aq. solution equilibrated with 1 × 10 ⁵ Pa CO_2 partial pressure Quaternary sand aquifer Injection depth 18 m 400,000 L of CO_2	n.d.	–21.9	n.d.	n.d.	–30.5	n.d.
Wittstock experimental site (Germany) Peter et al. (2012) Schulz et al. (2012)	Sandstone unit of the Frio formation 1500 m depth 1600 tonnes of CO_2	n.d.	–5	+0.8	n.d.	–35 to –51	n.d.
Frio Brine Pilot (Texas USA) Kharaka et al. (2006b)	Sandstone unit in the Stuttgart formation 620 m depth 60,000 tonnes of injected CO_2	n.d.	–4.2 to –20.1	–5.2 to –5.6	n.d.	–26.6 to –30.2	–8.7 to –29.3
Ketzin site (Germany) Myrtilinen et al. (2010a,b) Martens et al. (2012)							

n.d. = not determined.

^a CO_2 was injected in dissolved phase.

Lions et al., 2014b), since 50% of the C in the formed HCO_3^- originate from soil CO_2 and 50% from primary carbonates (Eq. (2)). Under reservoir conditions ($T > 50^\circ\text{C}$, $p > 10\text{ MPa}$, salinities $> 10,000\text{ mg/L}$), $\delta^{13}\text{C}$ values of DIC higher than -10‰ may be observed (Table 1) due to other CO_2 sources (e.g. crustal or mantle CO_2 under closed system conditions) or processes affecting the C isotope ratios of DIC (e.g. methanogenesis).

Formation waters and groundwaters typically have $\delta^{18}\text{O}$ values between -17 and 0‰ (Table 1) depending on geographic location of the site and extent of water–rock interactions of the formations waters. O isotope ratios of baseline CO_2 in formation waters and groundwaters are also controlled by the O isotope equilibria between H_2O and CO_2 that favours the enrichment of ^{18}O in the CO_2 (e.g. Bottinga, 1968; Epstein and Mayeda, 1953; Friedman and O'Neil, 1977; Mills and Urey, 1940). The amount of O in H_2O is typically orders of magnitude higher than the amount of O in baseline dissolved or free phase CO_2 . Hence, it has been shown that baseline CO_2 assumes $\delta^{18}\text{O}$ values that are between 28 and 42‰ higher than those of water dependent on temperature in accordance with known O isotope effects between H_2O and CO_2 (Johnson et al., 2011b).

Where possible, the temporal and spatial variability of the isotopic composition of baseline C compounds in the formations of interest should be determined prior to commencement of CO_2 injection. This is important in order to assess the variability of $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values of baseline compounds, against which subsequent changes due to CO_2 injection can be compared. Under ideal circumstances, this variability may be as low as $\pm 1\text{‰}$, but larger variabilities have been observed at several CCS sites (e.g. Johnson et al., 2011a,b; Mayer et al., 2013).

4.2. Isotopic composition of injected CO_2

Anthropogenic CO_2 emissions arise mainly from the combustion of fossil fuels during power generation and in the industrial and transport sectors. However, anthropogenic CO_2 is also emitted from non-combustion sources in industrial processes, such as cement manufacturing, natural gas processing and hydrogen production (IPCC, 2006). In many cases, captured CO_2 is derived from burning coal or petroleum, and hence often has $\delta^{13}\text{C}$ values ranging between -24 and -27‰ (Tans, 1981; Tissot and Welte, 1984). However, if injected CO_2 is derived from conversion of methane, its $\delta^{13}\text{C}$ value will usually be more negative than -35‰ (Tans, 1981). In contrast, if CO_2 occurs as a by-product during natural gas production its $\delta^{13}\text{C}$ value may be higher than -5‰ . Finally, mantle-derived CO_2 as utilized in EOR projects in Texas (USA) has $\delta^{13}\text{C}$ values around -6‰ . Hence, $\delta^{13}\text{C}$ values of injected CO_2 at different CCS field sites and pilot experiments have varied widely from values as low as -51.1‰ (dissolved phase CO_2 at Wittstock, Table 1) to as high as -4.7‰ (supercritical CO_2 at Pembina, Table 1) depending on the source of the injected CO_2 . $\delta^{18}\text{O}$ values of injected CO_2 varied from $< +2.5$ to $+28.6\text{‰}$ on the V-SMOW scale (Table 1). If injected CO_2 is always derived from the same source, it is possible that its $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values vary by less than $\pm 1.0\text{‰}$ throughout the duration of an injection project (e.g. Mayer et al., 2013). In contrast, if CO_2 is derived from different sources, significant variations in the isotopic composition of injected CO_2 may be observed, and if monitored properly, can be exploited for tracer studies.

Depending on the source of the injected CO_2 , the $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values are often markedly different from those of background compounds at storage sites. For instance, at the Pembina Cadium CO_2 -EOR pilot in Alberta (Canada), the injected CO_2 had a $\delta^{13}\text{C}$ value of -4.7‰ that was more than 10‰ higher than the $\delta^{13}\text{C}$ value of baseline C species. For experimental studies in Germany and the USA, the difference between C isotope ratios of injected CO_2 and those of baseline C compounds ($\Delta\delta^{13}\text{C}$) ranged between

10‰ (Peter et al., 2012) and 30‰ (Assayag et al., 2009a), respectively (Table 1). In cases where the stable isotope composition of injected CO₂ is sufficiently distinct, it can be used as a tracer for movement and reactions of CO₂ within the reservoir and during potential leakage, provided that isotope fractionation effects during CO₂ transport and reactions are small or known. In this case, mixing of injected CO₂ with pre-existing (e.g. baseline) carbon pools in the subsurface can be quantified via mass and isotope balances.

4.3. Quantifying movement and fate of injected CO₂

If the $\delta^{13}\text{C}$ value of injected CO₂ is sufficiently different from that of baseline CO₂ in the target reservoir, the arrival of injected CO₂ at an observation well in the reservoir, or monitoring wells in overlying strata, will cause systematic changes of $\delta^{13}\text{C}$ from baseline values towards that of the injected CO₂. Under the assumption that no C isotope fractionation or mixing processes alter the $\delta^{13}\text{C}$ value of the respective end-members, a mass balance can be described by the following mixing equation:

$$\delta^{13}\text{C}_{\text{mix}} \times m_{\text{mix}} = \delta^{13}\text{C}_{\text{bl}} \times m_{\text{bl}} \times (1 - X) + \delta^{13}\text{C}_{\text{inj}} \times m_{\text{inj}} \times X \quad (7)$$

where $\delta^{13}\text{C}$ and m denote the C isotope ratios and concentrations of injected (inj) and baseline (bl) inorganic carbon (CO₂ or DIC) and resulting mixtures (mix). X is the fraction of injected volume in the resulting mixture. Fig. 2 illustrates this two-source mixing concept (Eq. (7)) using monitoring data from four cases studies: the CO₂ enhanced oil recovery (EOR) projects at Weyburn in Saskatchewan (Canada) (Mayer et al., 2013) and at the Pembina Cardium CO₂ pilot project in Alberta (Canada) (Johnson et al., 2011b), the experimental aquifer injection sites at Wittstock in Germany (Peter et al., 2012; Schulz et al., 2012) and at Lamont-Doherty in the USA (Assayag et al., 2009b). The $\delta^{13}\text{C}$ values of injected CO₂ and of baseline C compounds for the 1500–1800 m deep CO₂ enhanced oil recovery (EOR) projects are summarized in Table 1. The $\delta^{13}\text{C}$ value of injected CO₂ at Weyburn was on average ~8‰ (Mayer et al., 2013) and in some cases 13‰ lower (Fig. 2a), and at Pembina ~12‰ higher (Fig. 2b) than those of baseline CO₂ in the reservoir. Regular monitoring at selected observations wells revealed a rapid increase (Pembina) or decrease (Weyburn) of $\delta^{13}\text{C}$ values of CO₂ obtained from the well casing with increasing CO₂ concentrations. The majority of the monitoring data plotted near the mixing line predicted by Eq. (7) indicating arrival of injected CO₂. Hence, assuming negligible C isotope fractionation, it is possible to quantitatively estimate the proportion of injected CO₂ at each sampling event.

Fig. 2c and d show $\delta^{13}\text{C}$ values of DIC for the Wittstock and Lamont-Doherty shallow aquifer injection experiments (Assayag et al., 2009a; Peter et al., 2012). For the Wittstock experiment, the $\delta^{13}\text{C}_{\text{DIC}}$ value of injected CO₂ dissolved in water was approximately 8‰ lower than that of baseline DIC (Fig. 2c), whereas for the Lamont-Doherty experiment the $\delta^{13}\text{C}_{\text{DIC}}$ value of injected CO₂ dissolved in water was 32‰ lower than that of baseline DIC (Fig. 2d). After CO₂ injection commenced at Wittstock, $\delta^{13}\text{C}$ values of DIC rapidly approached those expected for DIC derived from injection CO₂ while DIC concentrations increased (Fig. 2c) since the aquifer matrix was composed of medium to coarse sand free of carbonates. At the Lamont-Doherty experiment, the $\delta^{13}\text{C}$ values for DIC also decreased rapidly with increasing DIC concentrations, but plotted several ‰ above the expected mixing line (Fig. 2d). This indicates arrival and dissolution of injected CO₂, but also reveals an additional DIC source that was identified as calcite dissolution in the doleritic aquifer that was enhanced by the presence of newly formed H₂CO₃ (Assayag et al., 2009b).

When $\delta^{13}\text{C}$ values of baseline and injected CO₂ vary by less than $\pm 1.0\text{‰}$ (i.e. $\Delta_{x,y}$) respectively, the changes in the difference

between C isotope ratios can be determined with isotopic uncertainties of less than 1.4‰ (i.e. $\Delta_{\text{propag.}}$) according to the law of uncertainty propagation (Ku, 1966):

$$\Delta_{\text{propag.}} = \sqrt{\Delta_x^2 \times \left(\frac{\partial f}{\partial x}\right)^2 + \Delta_y^2 \times \left(\frac{\partial f}{\partial y}\right)^2} \quad \text{with } f(x, y) = x - y \quad (8)$$

Therefore, if the difference between $\delta^{13}\text{C}$ values of baseline and injected CO₂ is 10‰ or more, and isotope effects during CO₂ transport and reactions are either negligible or thoroughly known, then uncertainties in assigning proportions of injected CO₂ at observation wells within the reservoir or at monitoring wells in strata above the storage site can be made with uncertainties of less than $\pm 14\%$. At higher variabilities in the uncertainties of isotopic baseline values (e.g. $> \pm 2\text{‰}$) and smaller differences between the $\delta^{13}\text{C}$ values of baseline and injected CO₂ (e.g. $< 5\text{‰}$) it becomes more challenging to quantitatively determine proportions of injected CO₂ at monitoring wells, since the uncertainties increase to $> 2.8\%$ or $> 56\%$ of the difference between the $\delta^{13}\text{C}$ values. Therefore, a difference of 5‰ between the $\delta^{13}\text{C}$ values of injected CO₂ and those of C-containing baseline compounds is considered the minimum required for reliable application of the stable isotope tracer approach.

5. Processes with the potential to change the isotopic composition of injected CO₂

While the general principles for using the isotope compositions of injected CO₂ as a tracer are thoroughly known as described above, there are still several knowledge gaps regarding C and O isotope effects for the special conditions of CCS settings that may limit the applicability of the isotopic composition of CO₂ as a tracer. These current limitations are reviewed in this section and suggestions for closing the identified knowledge gaps are made.

5.1. Phase change from supercritical to subcritical CO₂

CO₂ is typically injected into the target reservoir in supercritical state. During potential leakage, the CO₂ may, however, reach pressure and temperature conditions under which a phase change to gaseous CO₂ occurs. The complete phase change of a given volume of CO₂ from supercritical to subcritical state or vice versa will have no effect on the isotope composition of the CO₂, since no C or O molecules are added or removed and hence no partitioning of isotopes between different phases can take place. However, it is necessary to explore whether partial phase changes are accompanied by isotope effects.

Initial laboratory investigations revealed no evidence of significant changes in C and O equilibrium isotope fractionation between supercritical CO₂ (CO_{2(sc)}) and H₂O (Johnson and Mayer, 2011) or DIC (Becker et al., in press) compared to CO_{2(g)} at similar temperatures but subcritical conditions (e.g. lower pressures). Johnson and Mayer (2011) investigated O isotope ratios as tracers for CO₂ in C storage reservoirs in a series of experiments, some of which reached supercritical conditions, without finding significant differences in O isotope fractionation between sub- and supercritical conditions. Rosenbaum (1997) derived O isotope partition function ratios for gaseous, liquid and supercritical CO₂ and H₂O revealing a similar isotope behaviour of gaseous and supercritical CO₂. Becker et al. (in press) also conducted laboratory experiments and evaluated C and O isotope effects between reservoir fluids and CO₂ at the transition between supercritical and subcritical CO₂, and found no significant deviations from the expected isotope effects regardless whether the CO₂ was in supercritical or subcritical state. Therefore, initial research conducted on isotope effects during the transition of CO₂

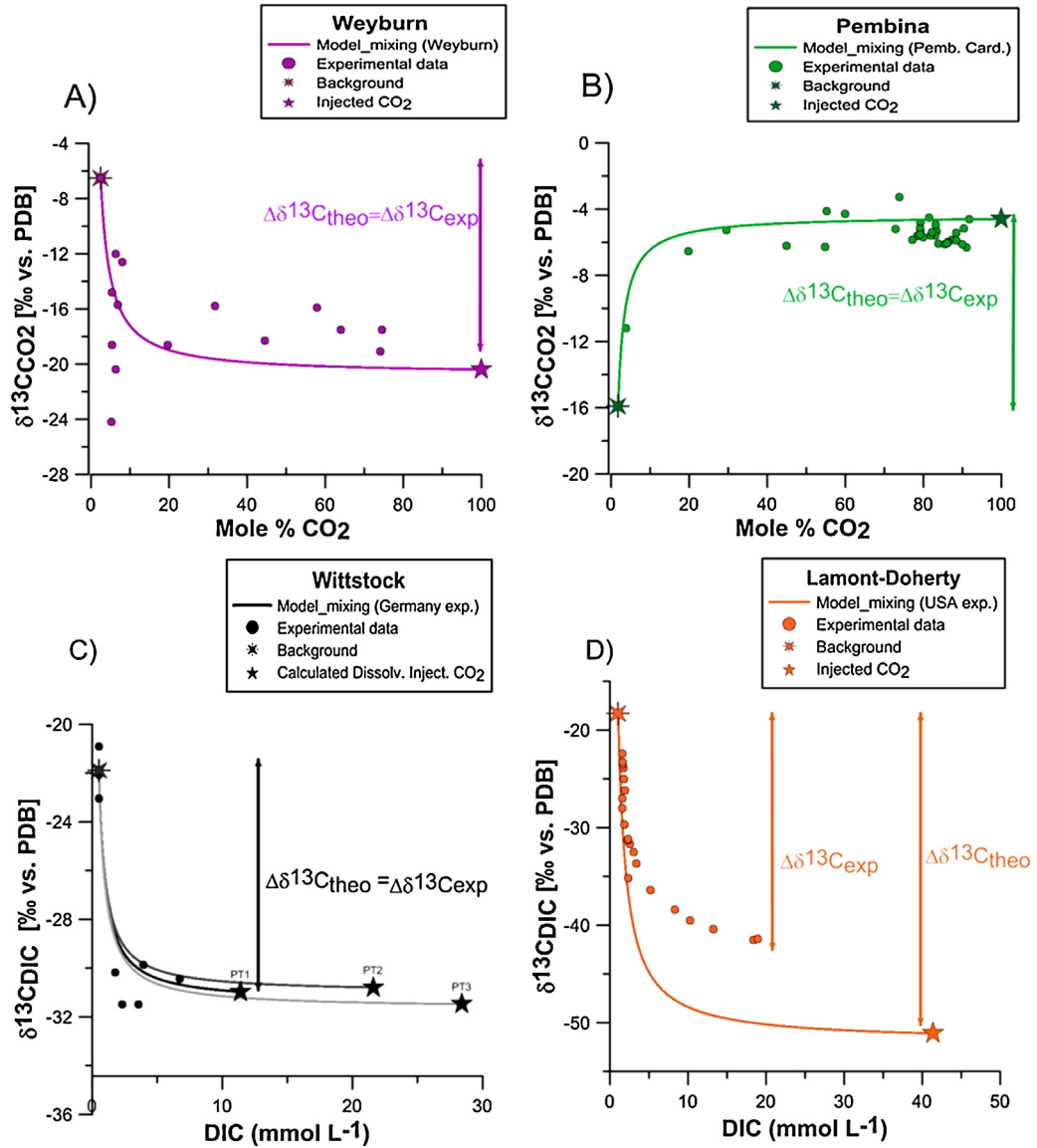


Fig. 2. Mixing of baseline and injected CO_2 or DIC at various CCS sites. Displayed are experimental results (data from Assayag et al., 2009b; Johnson and Mayer, 2011; Mayer et al., 2013; Peter et al., 2012) and theoretical mixing trends calculated for $\delta^{13}\text{C}$ of CO_2 for the Pembina Cardium and the Weyburn projects (Canada) and for $\delta^{13}\text{C}$ of DIC for the experimental sites in Germany and USA using Eq. (7). Note that for the study of Peter et al. (2012), the $\delta^{13}\text{C}$ value of dissolved injected CO_2 was calculated using PREEQC (Parkhurst and Appelo, 1999) for three different P_{CO_2} conditions (PT1, PT2, PT3) with a range from 0.3 to 1 bar and assuming equilibrium isotope fractionation between DIC species at 10 °C.

from sub- to supercritical state does currently not indicate significant (>1‰) additional isotope effects compared to those expected for subcritical CO_2 . Therefore, this phase change does not compromise the application of C and O isotope methods as a tool for monitoring movement and fate of injected CO_2 within the storage reservoir and during potential leakage. Due to the limited number of studies investigating isotope effects of supercritical CO_2 e.g. with DIC in reservoir brines, it is however strongly recommended to conduct further research on this topic.

5.2. Transport mechanisms

5.2.1. Effects of diffusion and advection on the isotopic composition of CO_2

Advective transport generally is assumed to not influence the isotope ratio of the transported compounds (Kayler et al., 2010). In contrast, stable isotope substitution within a gas affects its diffusion coefficients. Therefore isotope fractionation may occur because the

diffusion coefficients for $^{12}\text{CO}_2$ and $^{13}\text{CO}_2$ are not equal. For CO_2 , the slightly higher diffusion coefficient D of $^{12}\text{CO}_2$ compared to $^{13}\text{CO}_2$ indicates that $^{12}\text{CO}_2$ diffuses faster than $^{13}\text{CO}_2$. The diffusion velocity differential for these isotopologues may be as high as the inverse square root of the molecular masses m . For diffusion of $^{13}\text{CO}_2$ and $^{12}\text{CO}_2$ in air, this is described as:

$$\frac{D_{^{12}\text{CO}_2, \text{air}}}{D_{^{13}\text{CO}_2, \text{air}}} = \sqrt{\frac{m^* \times (m + m_{\text{air}})}{m \times (m^* + m_{\text{air}})}} \quad (9)$$

with m^* and m representing the molecular masses of $^{13}\text{CO}_2$ and $^{12}\text{CO}_2$ respectively. It has been demonstrated in 1-dimensional flow-through column experiments that the leading front of the CO_2 elution peak will have $\delta^{13}\text{C}$ values that may be several ‰ lower than those of the source CO_2 if the transport is diffusion dominated (Larson and Breecker, 2014). However, the same experiment demonstrated that the $\delta^{13}\text{C}$ value rapidly approached that of the source CO_2 within 1 h after the leading edge of the CO_2 had passed

the column exit. This suggests that no significant C isotope effects are expected in diffusion-dominated geological media once the diffusion front has passed. In a study of C isotope effects during diffusion in water, Zeebe (2011) found no significant carbon isotope fractionation for HCO_3^- and CO_3^{2-} ions and only a small isotope effect for $\text{CO}_{2(\text{aq})}$ of $\sim 0.7\%$ at 25°C . This value is in agreement with earlier studies (Jahne et al., 1987; O'Leary, 1984) indicating negligible isotope effects once the leading edge of the diffusion front has passed.

For tracing CO_2 leakage in the near-surface environment, e.g. above shallow aquifers, CO_2 diffusion through the water-unsaturated soil zone must also be considered. The ratio of the diffusion coefficients $D_{12\text{CO}_2}/D_{13\text{CO}_2}$ of $^{12}\text{CO}_2$ and $^{13}\text{CO}_2$ in soil air is 1.0044 (Eq. (9)), which results in a maximum isotopic enrichment (ϵ) of -4.4% (Amundson et al., 1998; Cerling et al., 1991; Craig, 1953; Jost, 1953). The relevance of this diffusion-based isotope fractionation for CO_2 leakage detection depends on the monitoring scenario. Large scale point leaks, e.g. along well bores, are assumed to be dominated by advection processes induced by the pressure differences between reservoir and overlying formations and thus would not give rise to diffusional isotope fractionation. For stable isotope monitoring at soil level, the C isotope fractionation of up to -4.4% has to be taken into account, if diffusive CO_2 flux from shallow groundwater into the overlying soil zone occurs. In this case it may be preferable to monitor aquifers or soil gas below the topsoil zone.

During diffusion, there may be significant isotope effects at the leading edge of the CO_2 plume causing enrichment of the light isotope ^{12}C . Hence, the leading edge of the CO_2 plume may have lower $\delta^{13}\text{C}$ values than the injected CO_2 if diffusion is a dominant process. However, the isotopic composition of the diffusing CO_2 rapidly returns to the isotopic composition of the injected CO_2 as CO_2 fluxes increase. Therefore, diffusion is not expected to compromise the usefulness of the isotopic composition of CO_2 as a tracer once the potentially diffusion-dominated leading edge of the plume has passed.

5.2.2. Effects of multi-component-phase flow on the isotopic composition of CO_2

Injection of CO_2 into a storage reservoir usually results in multi-component-phase flow involving saline reservoir water and supercritical CO_2 , as well as oil in EOR scenarios. The residual gas saturation is a key parameter that determines CO_2 and water velocities in the vicinity of an injection well. The different relative permeabilities of saline reservoir water and supercritical CO_2 combined with isotope effects during dissolution and dissociation of injected CO_2 (Johnson et al., 2011b) may result in isotopic patterns at observation wells that deviate from a two end-member mixing model especially at the fringe zones of the CO_2 plume as suggested by modelling-based research by Zhang et al. (2014). Further field-based research on these phenomena is highly recommended, although it is expected that deviations from two end-member mixing models will rapidly decrease once the majority of the CO_2 arrives at an observation well (e.g. Johnson et al., 2011b).

5.3. Isotope effects due to geochemical reactions

5.3.1. Temperature effects on isotope fractionation during CO_2 dissolution and dissociation

5.3.1.1. Carbon isotope effects between CO_2 and DIC. Dissolution of injected CO_2 into formation water and subsequent dissociation of H_2CO_3 into HCO_3^- and H^+ is accompanied by C isotope fractionation that strongly depends on the pH values of the solution and the resulting distribution of dissolved C species at any given temperature, pressure and salinity condition in the subsurface (see Section 2). At acid to neutral pH conditions in formation waters

within and above the CO_2 injection reservoir, isotope fractionation between CO_2 , H_2CO_3 and HCO_3^- are the most relevant processes for monitoring purposes (Becker et al., 2011). Temperature-dependent equilibrium isotope fractionation between $\text{CO}_{2(\text{g})}$, H_2CO_3 , and HCO_3^- controls the $\delta^{13}\text{C}_{\text{CO}_2}$ and $\delta^{13}\text{C}_{\text{DIC}}$ values. Myrntinen et al. (2012) reviewed previously published carbon isotope fractionation relations between CO_2 and DIC and reported that experimentally derived temperature dependent C isotope fractionation equations have only been reliably determined between CO_2 and H_2CO_3 up to 60°C (Vogel et al., 1970), between CO_2 and HCO_3^- up to 70°C (Mook et al., 1974) and between CO_2 and CO_3^{2-} up to 40°C (Halas et al., 1997). These data were, however, generated in experiments conducted at or near atmospheric pressures and often at temperatures lower than those encountered at many CO_2 storage sites. Therefore, Myrntinen et al. (2014) have recently determined C isotope fractionation between CO_2 and H_2CO_3 at temperatures up to 120°C and pressures relevant for CO_2 storage sites and leakage scenarios. They found that C isotope fractionation between CO_2 and H_2CO_3 decreases from about -1.2% at room temperature to -0.7% at 120°C at elevated pressures (5.5 MPa). This C isotope fractionation is highly predictable, decreases with increasing temperature, and is smaller than at near-surface conditions, which is favourable for C isotope tracer approaches. Further high pressure and high temperature data are, however, necessary especially for C isotope fractionation between CO_2 and HCO_3^- .

5.3.1.2. Oxygen isotope effects between CO_2 and H_2O . Temperature-dependent O isotope equilibrium fractionation between CO_2 and H_2O has previously been determined at atmospheric pressures and temperatures of up to 100°C as described by Bottinga (1968):

$$10^3 \ln \alpha^{18}\text{O}_{\text{CO}_{2(\text{g})}-\text{H}_2\text{O}} = -0.0206 \times 10^6 T^{-2} + 17.9942 \\ \times 10^3 T^{-1} - 19.97 \text{‰} \quad (10)$$

with the temperature T given in Kelvin. This equation indicates that the $\delta^{18}\text{O}$ value of CO_2 is 40.15% at 25°C higher than the $\delta^{18}\text{O}$ value of H_2O . This difference decreases with increasing temperatures (e.g. 31.6% at 75°C). Becker et al. (in press) have conducted CO_2 – H_2O equilibrium experiments at elevated temperatures and pressures relevant for CO_2 storage sites and found oxygen isotope fractionations within 1% of those reported by Bottinga (1968). Furthermore, these authors demonstrated that the extent of oxygen isotope fractionation between CO_2 and H_2O was similar for supercritical and subcritical CO_2 . Therefore, previously reported oxygen isotope effects between CO_2 and H_2O should also apply at elevated temperature and pressure conditions of CO_2 storage sites.

When assessing the oxygen isotope behaviour of injected CO_2 , it is, however, important to consider the relative proportions of oxygen-containing compounds at various depths. At low pressures typical for near-surface conditions, the large amount of O in the water molecules will control the O isotope ratio of CO_2 and hence the $\delta^{18}\text{O}$ value of CO_2 will adjust to the oxygen isotope ratio of the H_2O and the isotope fractionation factor (α) appropriate for the given temperature (Eq. (10)). Within the CO_2 storage reservoir, supercritical CO_2 may however represent the dominant oxygen pool in the CO_2 – H_2O system. While equilibrium isotope fractionation between CO_2 and H_2O remains governed by Eq. (10), it is now possible that the $\delta^{18}\text{O}$ values of the formation water adjust partially to that of the injected CO_2 (Johnson and Mayer, 2011). Consequently, it has been demonstrated that changes in $\delta^{18}\text{O}$ values of reservoir water have the potential to indicate presence of, and pore space saturation with injected CO_2 . This has been demonstrated in the Pembina Cardium CO_2 monitoring and the Frio projects (Johnson et al., 2009; Kharaka et al., 2006b). The study of Johnson et al. (2011a) demonstrated that the extent of change in the $\delta^{18}\text{O}$

values of reservoir water due to equilibrium isotope exchange with injected CO₂ depends on the amount of CO₂ present. Therefore, changes in the δ¹⁸O values of formation water due to CO₂ injection are most likely observed within the storage reservoir where pore-space saturation with supercritical CO₂ is high. In contrast, such changes are unlikely if small amounts of sub- or supercritical CO₂ leak into overlying shallow aquifers.

5.3.2. Salinity effects on the isotopic composition of CO₂

Since the salinities of waters in CO₂ injection formations and overlying formations and aquifers can vary from more than 250,000 mg/L to less than 5000 mg/L it is important to understand the influence of water salinity on C and O isotope fractionation. The influence of salinity on C isotope fractionation between CO₂ and DIC is believed to be negligible although the number of studies investigating this effect is limited. However, there is evidence for a measurable influence of salinity on O isotope fractionation between CO₂ and H₂O. The influence of salinity on gas solubility and associated isotope effects is often described as the salt-effect (Horita et al., 1993). Multiple studies (Fortier, 1994; Kazahaya, 1986; O'Neil and Truesdell, 1991; Sofer and Gat, 1972) have confirmed that the differences between δ¹⁸O values of CO₂ and H₂O in saline solutions relative to the O isotope fractionation factor determined for pure water are slightly higher than analytical precisions (±0.2‰). For instance, Lécuyer et al. (2009) investigated O isotope fractionation between CO₂ and H₂O at 313 K (~40 °C) and atmospheric pressure for salinities ranging from 0 to 250 g/L and found both an influence of salinity and an increase of the isotopic equilibration times. The difference to fresh-water O isotope fractionation factors increased with salinity, showing an offset of only +0.15‰ at salinities of 35 g/L but differences of +0.4 to +0.6‰ at salinities between 100 and 250 g/L at temperatures of 40 °C. Salt composition (e.g. KCl vs. NaCl) did not affect the extent of O isotope fractionation between CO₂ and H₂O (Lécuyer et al., 2009). In contrast, Horita et al. (1995) found an increasing influence of salinity on O isotope fractionation between H₂O and CO₂ above 200 °C, but disputed a significant salinity effect below this temperature. Although no studies investigated the combined influences of pressure, temperature and salinity on C and O isotope fractionation between CO₂, H₂O and DIC relevant for CO₂ storage conditions, we conclude that salinity effects appear to be negligible for C isotopes and small (<1‰) for O isotope ratios of CO₂. While further detailed studies of salinity, *T* and *p* effects on the isotopic composition of CO₂ in storage scenarios are recommended, there is currently no evidence that these effects would significantly compromise the suitability of the stable isotopic composition of injected CO₂ as a tracer tool.

5.3.3. Non-equilibrium effects of degassing

As described in Section 2.3, degassing of CO₂ from aqueous solutions occurs via carbonate equilibria reactions ($\text{H}^+ + \text{HCO}_3^-(\text{aq}) \xrightleftharpoons{K_2} \text{H}_2\text{CO}_3 \xrightleftharpoons{K_1} \text{CO}_2 + \text{H}_2\text{O}$). These processes are relevant for monitoring CO₂ storage sites, but have also been previously investigated for air–seawater CO₂ exchange (Clark and Lauriol, 1992), CO₂ degassing from hydrothermal fluids (Gaillardet and Galy, 2008), and carbonate equilibria of surface waters influenced by CO₂-rich groundwater (Doctor et al., 2008). Degassing of CO₂ from fluids causes equilibrium or kinetic (non-equilibrium) C isotope fractionation (Clark and Lauriol, 1992; Marlier and O'Leary, 1984; Zeebe and Wolf-Gladrow, 2001) depending on degassing rate. If degassing of CO₂ from a fluid into an adjacent gaseous phase is slow (i.e. less than half the bicarbonate in solution converted to CO₂ (and possibly CaCO₃) in 2000 s), C isotopic equilibrium fractionation between DIC and the outgassing CO₂ occurs (Section 5.3.1). At rapid degassing rates (i.e. more than half the bicarbonate in solution is converted to CO₂ (and possibly CaCO₃) in 2000 s),

kinetic isotope fractionation occurs and influences the isotopic composition of both degassed CO₂ and DIC (Hendy, 1971). Zhang et al. (1995) reported a minor kinetic fractionation for C isotopes of less than 1‰ during outgassing of CO₂ from water at temperatures between 5 and 21 °C.

The impact of isotope effects during outgassing on the isotopic composition of CO₂ depends on the leakage scenario. As long as the injected CO₂ is fully contained in the storage reservoir under a competent caprock, no outgassing occurs. If there is leakage from the storage reservoir along an imperfectly sealed injection well (Fig. 1) from a plume of supercritical CO₂ in contact with saline waters with a pH value <5 where DIC occurs dominantly as H₂CO₃, isotopic fractionation is expected to generate leaking CO₂ that has a δ¹³C value at most 1‰ lower than that of the injected CO₂ (Fig. 3), especially if leakage rates are slow. At fast leakage rates, leaking CO₂ is expected to be isotopically almost identical to that of injected CO₂. Therefore, casing gas samples obtained from injection or observation wells are believed to yield CO₂ that is isotopically representative for the CO₂ outgassing from the storage formation (e.g. Johnson et al., 2011b).

When leaking CO₂ reaches shallow aquifers that overly storage formations, and the environmental boundary conditions change from confined towards unconfined conditions or towards elevated pH values, degassing with associated carbon isotope effects may occur. While the δ¹³C values of outgassing CO₂ is still expected to be only about 1‰ lower than that of H₂CO₃, the remaining DIC becomes initially enriched in ¹³C. Under unconfined near-surface conditions, outgassing of CO₂-charged waters will continue until chemical equilibrium with near-surface conditions is reached. Under such conditions, the progressive enrichment in ¹³C can lead to increasing δ¹³C values of the remaining DIC. If the resulting gas phase is removed continuously from fluid contact, the preferential loss of ¹²CO₂ will result in enrichment of ¹³C in the remaining DIC. For instance, Doctor et al. (2008) observed increases in the δ¹³C values of stream DIC that ranged between 2 and 5‰ due to outgassing of CO₂ from infiltrating groundwater with excess aqueous partial pressures of CO₂ that were up to 20 times the value of the atmosphere. Possible CO₂ excess pressures during leakage above CO₂ storage sites may be much higher and may thus impart different cumulative isotope effects. Presumably, rapid degassing may cause smaller isotope shifts after pressure changes occur due to non-preferential isotope selection under steep pressure gradients. In contrast, slow outgassing of CO₂ over longer time periods especially in near-surface unconfined aqueous systems may impart significant ¹³C-enrichments in the remaining DIC. This must be considered during monitoring of CO₂ storage sites in shallow aquifers. Further research is recommended to better quantify effects of outgassing of CO₂ under various boundary conditions with different water salinity, pH, DIC content and starting partial pressures of CO₂.

The issue of isotope effects during outgassing of CO₂ is also of relevance for fluid sampling from CO₂ storage sites. Down-hole devices that return fluid samples under pressurized conditions prevent outgassing of CO₂ and hence are preferred. Samplers that do not prevent outgassing of CO₂ during return of the sample to the surface may have their fluids subject to non-equilibrium degassing processes that may impart isotope effects. Therefore, Myrntinen et al. (2010a) recommended the use of pressure-tight down-hole samplers when possible. Where this is not technically possible, care must be taken to minimize outgassing of CO₂ during sampling in order to preserve the integrity of the isotopic composition of the investigated carbon compounds.

5.3.4. Non-equilibrium effects during CO₂ dissolution

The time required to reach isotopic equilibrium is generally longer than the time required to achieve chemical equilibrium (Uchikawa and Zeebe, 2012). Nevertheless, C isotope equilibrium between CO₂ and DIC is usually established within hours

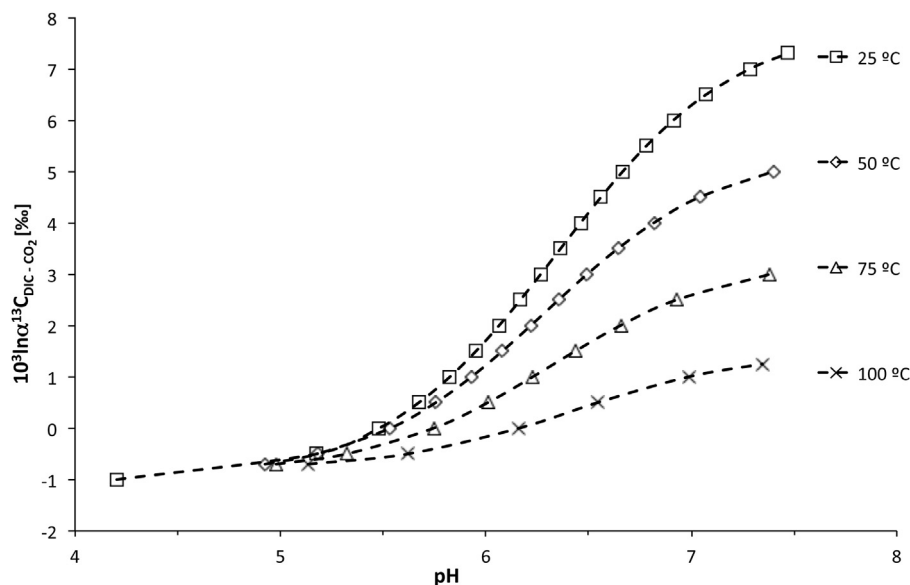


Fig. 3. The difference between $\delta^{13}\text{C}$ values of CO_2 and various DIC species at atmospheric pressure, dependent on pH value of the solution and temperature modelled and modified after Myrntinen et al. (2015).

(Myrntinen et al., 2015) and hence C isotope non-equilibrium effects are of no relevance for CO_2 monitoring scenarios. In contrast, O in CO_2 is not only exchanged with DIC species, but also with O in water (Uchikawa and Zeebe, 2012). Water constitutes a much larger O reservoir than DIC leading to noticeably longer equilibration times for O isotopes between CO_2 and H_2O . Exact equilibration times depend on gas/liquid ratios, contact areas, and the ambient conditions of the system including temperature, $p\text{CO}_2$ and salinity. Decreasing CO_2 solubility at higher temperatures inhibits the exchange of CO_2 with DIC and H_2O and thus increases chemical and isotope equilibration times (Becker et al., 2011). Elevated salinity has also been shown to increase isotope equilibration times with CO_2 in different experimental setups (Johnson and Mayer, 2011; Lécuyer et al., 2009). Rate constants for O isotope exchange have been reported to be smaller by an order of magnitude for 4 M solutions compared to solutions with lower (0.5 M) salinity (Fortier, 1994). A similar range of rate constants was found by Horita (1989) for different near-saturated salt solutions with KCl solutions having the highest and MgSO_4 solutions having the lowest rates. Lécuyer et al. (2009) found a three-fold increase of equilibration times from 4 to 12 h in a controlled automated sample preparation system at

atmospheric pressure, but fluid and gas volumes were not reported. Johnson and Mayer (2011) reported O isotope equilibration times between CO_2 and H_2O of up to one week for their experimental setup, although they applied pressures of up to 19 MPa and shook samples daily. This was recently confirmed by Becker et al. (in press), who reported O equilibration times between CO_2 and H_2O of up to 6 days using similar experimental setups under various pressure and temperature conditions, ranging from 22 to 86 °C and 1.0 to 8.8 MPa. This indicates that it may take up to one week to attain O isotope equilibrium between injected or leaking CO_2 and H_2O dependent on the mass ratios of CO_2 and water in or above storage reservoirs and the contact times between CO_2 and water. Prior to reaching equilibrium, kinetic oxygen isotope effects also preferentially apportion ^{18}O into CO_2 and the isotopic enrichment factor between CO_2 and H_2O approaches the equilibrium values shown in Fig. 4 with time. The equilibration times between oxygen isotopes in CO_2 and saline reservoir water may be relevant for reservoir monitoring with $\delta^{18}\text{O}$ values especially during the first days of plume detection depending on the flow conditions in the reservoir or during leakage, but after a few days oxygen isotope equilibrium between CO_2 and H_2O will be attained.

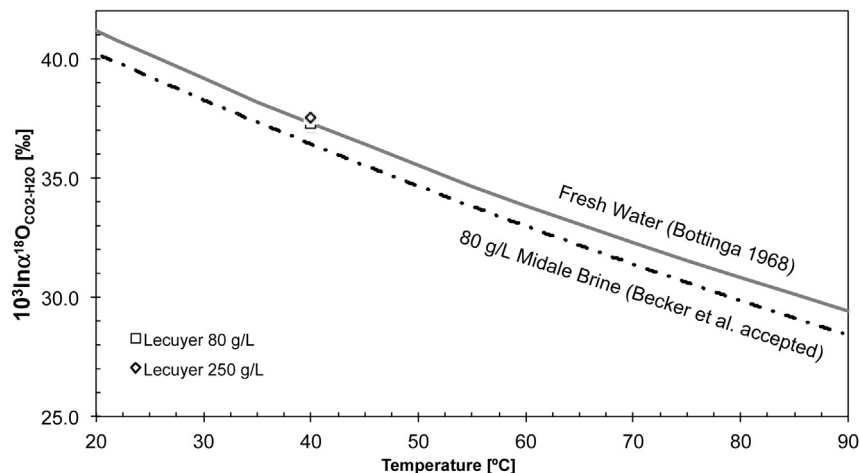


Fig. 4. The difference between $\delta^{18}\text{O}$ values of CO_2 and H_2O for freshwater according to Bottinga (1968) and for various saline solutions (Becker et al., in press; Lécuyer et al., 2009).

For monitoring CO₂ movement in storage reservoirs and potential CO₂ leakage from such sites using C isotope ratios of injected CO₂, equilibrium isotope conditions will be achieved at time scales of less than a day. In contrast, oxygen isotope ratios of injected CO₂ are not a conservative tracer since oxygen isotope exchange between H₂O and CO₂ impacts the $\delta^{18}\text{O}$ values of CO₂ initially via kinetic isotope effects, while approaching equilibrium isotope conditions within 7 days or less. Whether oxygen isotope equilibrium will be achieved depends on the contact time between CO₂ and H₂O and temperature, pressure and salinity conditions. Within the storage reservoir oxygen isotope equilibrium is expected to be attained within a few days. During CO₂ leakage scenarios, it will depend on the CO₂–H₂O contact times whether O isotope equilibrium will be reached or whether non-equilibrium isotope effects must be considered.

5.3.5. Effects of CO₂–water–rock interactions on the isotope composition of CO₂

It is of paramount importance to assess potential water–rock interactions affected by injected or leaking CO₂ since such reactions may have a significant impact on the isotopic composition of CO₂. The extent of CO₂–induced water–rock reactions depends strongly on the lithology of the reservoir and that of overlying formations in case of leakage. It also depends on the amount of CO₂ present, its contact time with formation waters and the rock matrix. Knowledge of the mineralogical and isotopic composition of the formation rocks that are in contact with injected or leaking CO₂ is therefore important.

5.3.5.1. Mineral dissolution. As shown in Section 2.3, the presence of CO₂ and H₂CO₃ will enhance carbonate mineral dissolution and will produce additional HCO₃[−] (Eqs. (2) and (3)), depending on the pH of the solution. Because the kinetics of carbonate dissolution are typically fast (Palandri and Kharaka, 2004), it is important to consider the impact of this reaction on the isotopic composition of CO₂. Since primary marine carbonates typically have $\delta^{13}\text{C}$ values of $+2 \pm 4\text{‰}$ (Veizer et al., 1999), their dissolution will produce additional DIC with $\delta^{13}\text{C}$ values that are markedly higher than that of most injected CO₂. Because the dissolution of carbonate minerals cannot selectively mobilize different isotopes from the mineral surface, no C isotope fractionation will occur during this process. Therefore, changes in the $\delta^{13}\text{C}$ values of DIC can be estimated by isotope mass balances that consider the DIC derived from CO₂ injection and that derived additionally from carbonate dissolution. The $\delta^{13}\text{C}$ value of DIC will be dominated by that of injected CO₂ at high injection and leakage rates. Only at the fringes of the CO₂ plume, or during CO₂ leakage at low rates will there be sufficient DIC derived from carbonate dissolution to cause increases in the $\delta^{13}\text{C}$ values of the resulting DIC by several ‰. This effect must be considered when using the carbon isotope ratio of CO₂ as a tracer especially in carbonate-containing reservoirs or overlying aquifers.

Dissolution or hydrolysis of silicate minerals is kinetically a slow process that is facilitated by the presence of carbonic acid derived from injected CO₂. Hence, its impact on the isotopic composition of CO₂ within and above CO₂ storage reservoirs is often negligible.

5.3.5.2. Mineral precipitation. Precipitation of carbonate minerals is a desirable long-term storage pathway for injected CO₂ that is often referred to as mineral trapping. If carbonate mineral precipitation is rapid, then the $\delta^{13}\text{C}$ value of the mineral will be similar to that of DIC in the aqueous solution. However, if mineral precipitation occurs slowly, the mineral will become slightly enriched in ^{13}C . However, since the amount of carbon allocated into minerals is usually very small compared to the amount of C remaining in dissolved or free phases, mineral precipitation is not expected to have

a noticeable effect on the isotopic composition of the CO₂ in the storage reservoir or leaking towards the near-surface environment.

5.3.5.3. Sorption processes during CO₂–coal interaction. If leaking CO₂ enters formations with coal seams, it may also be necessary to consider the effects of CO₂ sorption for instance on organic matter or clay minerals. It has been reported that sorption can cause changes of $\delta^{13}\text{C}$ values of CO₂ and the magnitude of the carbon isotope partitioning is comparable between different sorption studies (Bacsik et al., 2002; Larson and Breecker, 2014; Strapoc et al., 2006; Xia and Tang, 2012). These studies revealed that ^{12}C -enriched CO₂ is preferentially sorbed on the solid phase leading to progressively ^{13}C -enriched residual CO₂ along the flow path often following a Rayleigh fractionation effect (Clark and Fritz, 1997; Gonfiantini and Pennisi, 2006). During subsequent desorption, ^{12}C is preferentially released into the free gas phase. Such isotope effects during sorption are likely most relevant for dry geological substrates at dynamic flow conditions, while they often become negligible at water-saturated conditions as those inhibit the direct contact of CO₂ with the solid phase.

6. Conclusions

The isotopic composition of CO₂ can serve as a suitable tracer at large CO₂ injection sites provided that the injected CO₂ is isotopically distinct. Favourable conditions for this tracer approach exist if $\delta^{13}\text{C}$ values of injected CO₂ are more than 10‰ different compared to those of baseline C (CO₂, DIC) at the CCS site. In this case, changes in $\delta^{13}\text{C}$ values accompanied with increasing concentrations of CO₂ or DIC in samples obtained regularly at monitoring sites allow assessment of CO₂ plume distribution in the target formation and tracking potential leakage of CO₂ outside the storage reservoir. The proportion of injected CO₂ contributing to the obtained samples can be quantified with uncertainties of less than $\pm 20\%$ under the assumption that C isotope fractionation effects are either negligible or thoroughly known. Additional C isotope effects during phase change, transport and geochemical reactions under temperature, pressure and salinity conditions relevant for CO₂ storage sites may occur and deserve further investigations. Based on current information, these effects are expected to remain in most circumstances smaller than $\pm 2\%$ and therefore C isotope ratios remain an excellent tracer. Future investigations should focus on further assessing C and O isotope effects during phase change and reactions involving supercritical CO₂, and on effects of multicomponent-phase flow on the isotopic composition of CO₂. Further investigations regarding isotope effects during degassing and diffusion of CO₂ are also required especially for tracing leakage of CO₂. Finally, further detailed studies on the combined effects of salinity, temperature and pressure on the isotopic composition of CO₂ in storage reservoirs with different lithologies would be desirable to better quantify the impact of water–rock interactions on the isotopic composition of injected CO₂.

Based on current knowledge we suggest that the C isotope composition of injected CO₂ is a suitable tracer for the fate of CO₂ in the reservoir and for leakage detection at CO₂ storage sites provided that the $\delta^{13}\text{C}$ value of injected CO₂ is isotopically distinct from those of baseline C compounds. Oxygen isotope ratios of injected CO₂ are not a conservative tracer due to rapid O isotope exchange between CO₂ and water. $\delta^{18}\text{O}$ measurements on CO₂ and H₂O have, however, been shown to reveal pore-space saturation with CO₂. Hence, $\delta^{18}\text{O}$ values may also indicate presence of injected CO₂ within CO₂ storage reservoirs. CO₂–water–rock reactions can have a significant impact on the isotopic composition of CO₂ leaking from storage reservoirs. Therefore, careful evaluation

of site-specific conditions and processes is recommended if the isotopic composition of CO₂ is used as a tracer for CO₂ movement and potential leakage.

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