A Brief Overview of Isotope Measurements Carried Out at Various CCS Pilot Sites Worldwide

Martin Nowak[1], Anssi Myrttinen[1], Robert van Geldern[1],
Veith Becker[1,2], Bernhard Mayer[2], and Johannes A.C. Barth[1]

[1] GeoZentrum Nordbayern, Friedrich-Alexander-Universität Erlangen Nürnberg,
Angewandte Geologie, Schlossgarten 5, 91054 Erlangen, Germany
[2] Applied Geochemistry Group, Department of Geoscience, University of Calgary,
2500 University Drive N.W., Calgary, Alberta, Canada T2N 1N4

Abstract. About 1800 geochemical measurements including more than 1000 isotope analyses have been published as a result of geochemical monitoring programs established at several CO_2 storage and enhanced oil and gas recovery projects worldwide. These projects are briefly discussed here in order to compare sampling techniques to obtain fluid and gas samples for chemical and isotopic analyses. In all the projects, changes of stable isotope ratios of CO_2 and dissolved inorganic carbon in samples obtained pre- and post-injection were used to quantify solubility and ionic trapping of CO_2 via stable isotope mass balances. Further applications include, monitoring of underground CO_2 migration and early detection of potential CO_2 leaks into overlying formations. Other benefits of these stable isotope tracers include a better understanding of water-rock-gas interactions with CO_2 under supercritical conditions and often highly saline reservoir fluids that are present in the storage formations. While the results of these projects need further laboratory and experimental confirmation, further increase in field applications of stable isotope tracer techniques are anticipated with the introduction of new portable laser stable isotope mass spectrometers.

Keywords: Carbon capture and storage (CCS), enhanced oil and gas recovery (EOR and EGR), stable isotope monitoring, down-hole sampling.

1 Introduction

Well-based monitoring has been applied for several decades in the oil and gas industry to provide information for economic and safe extraction of hydrocarbons from the subsurface [1]. However, for verifying the storage of CO_2 in carbon capture and storage (CCS) and enhanced oil or gas recovery (EOR and EGR) projects these monitoring methods need to be further refined because CO_2 is mostly injected in a supercritical form resulting in potential geochemical rock-water-brine interactions and pressure changes [2,3]. This may lead to a

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mobilization of organic matter, trace elements and mineral dissolution that may affect subsurface geochemical compositions. Most downhole and surface sampling techniques applied so far focus on the geochemical assessment of liquid and gas samples and more recently also on stable isotope measurements [4-8].

Stable isotope ratios of carbon, oxygen and hydrogen are applied routinely to quantify interactions between the atmosphere, biosphere and geosphere [9]. The principle of stable isotope applications is that the naturally occurring variations of isotope abundances are useful tracers for phase changes, mobility and mixing of materials. For instance, if stable isotope ratios of fresh-water or dissolved carbon, remain unaltered, they can indicate various sources and enable mixing calculations. On the other hand, stable isotope ratios may change due to environmental processes including evaporation, diffusion as well as chemical or biological turnover of organic matter. If these isotope ratio changes (i.e. fractionations) are systematic, they can help to differentiate and quantify processes. By convention, natural stable isotope ratios are expressed in a per mille (‰) deviation from an internationally accepted standard, e.g. for the $^{13}C/^{12}C$ ratio according to the following equation:

$$\delta^{13}C \quad [‰] = (R_{\text{sample}}/R_{\text{reference}} - 1) \times 1000 \tag{1}$$

In this case, the international reference material is known as Vienna Pee Dee Belemnite (V-PDB).

At several CCS, EOR or EGR sites, isotope measurements have been applied successfully to monitor the distribution and mixing of injected CO_2 in the subsurface (Fig. 1). These isotope measurements include the determination of stable carbon ($^{13}C/^{12}C$) as well as oxygen isotope ratios ($^{18}O/^{16}O$) in order to quantify solubility trapping as dissolved inorganic carbon (DIC) and/or to trace

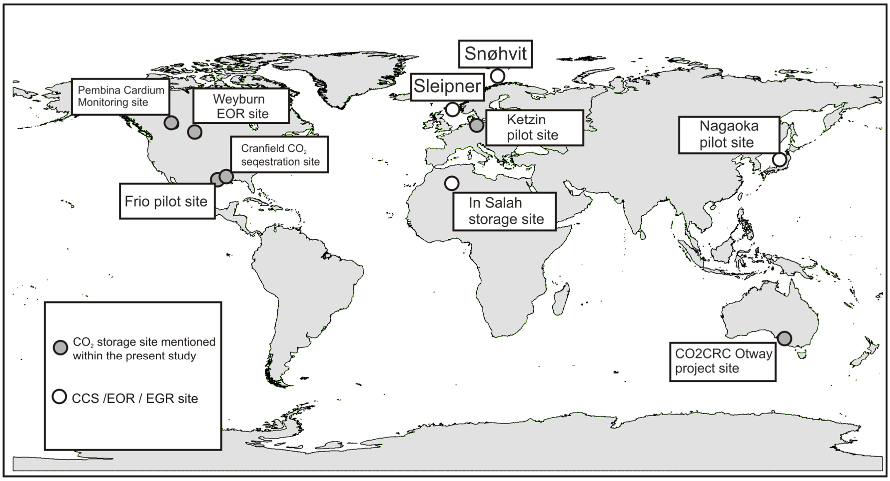

Fig. 1 Overview over selected CCS / EOR / EGR projects world-wide [11]

CO_2 breakthrough at observation wells [10,11,4]. Stable isotope values also allow the tracing of CO_2 migration [12] and can indicate saturation conditions of porous media with free-phase-CO_2 [13, 14]. The objective of this manuscript is to review and discuss selected published stable isotope applications in CO_2 storage projects worldwide. The goal is to review differences in sampling and monitoring strategies in order to reveal advantages and limitations of this innovative tracer approach and to outline the usefulness of these methods for future applications.

2 Overview of Isotope Applications in CCS Projects

2.1 The Weyburn Study

In Weyburn (Saskatchewan, Canada) isotope measurements were performed within the framework of a large scale monitoring program for a CO_2 enhanced oil recovery project to obtain baseline values from a carbonate reservoir before injection and to monitor the movement and the fate of CO_2 in the reservoir over a 10-year injection period [15]. After the start of CO_2 injection, continuous stable isotope monitoring of casing gas CO_2 revealed the movement of CO_2 in the reservoir. Furthermore, $\delta^{13}C$ measurements on dissolved inorganic carbon (DIC) enabled quantification of CO_2 dissolution (i.e. solubility trapping) [2,10]. Initial sampling took place between August 2000 and March 2001 and yielded 87 samples from production observation wells. Within this time span, more than 350 million m^3 of CO_2 was injected as miscible fluid, in order to enhance oil production [5]. Within the first monitoring campaign, the $\delta^{13}C$ value of DIC in fluid samples showed hardly any variance, although the injected CO_2 was depleted in ^{13}C compared to the baseline values (Tab. 1) [2]. This was attributed to calcite dissolution within the carbonate reservoir [16]. Further isotope studies that were conducted over a 40-month period after the commencement of CO_2 injection revealed increases in DIC concentrations and decreases in $\delta^{13}C$ values in the reservoir DIC [10]. Isotope mass balances allowed the assessment of the extent, to which increasing DIC was caused by solubility trapping of injected CO_2 and by mineral dissolution (Tab. 2) [10]. In this project that was conducted in a fully operational oil field, gas and fluid samples were collected at wellheads. This implies that the gas samples represented casing gas that consisted of a mixture of reservoir gases ascending to the wellhead and gases exhaled from the wellbore fluids. A total of 29 samples were analyzed for DIC (i.e. HCO^{3-}) concentrations and corresponding $\delta^{13}C$ values (Tab. 1), from the four wells reported in [10] but many more analyses were conducted throughout the 10-year duration of this project [15].

2.2 The Frio Experiment

During the Frio experiment in Texas, an integrated monitoring program was performed to investigate water-rock-interactions caused by 1600 tonnes of CO_2

that was injected into a saline sandstone aquifer [17]. The experiment aimed to explore the potential of injecting larger amounts of CO_2 and to evaluate associated geochemical reactions. For this purpose, an injection well was constructed and screened at about 1500 m depth below the ground surface. Advancements in sampling of fluids and gas were achieved by installing a U-tube sampling system in an observation well at a lateral distance of 30 m from the injection well. The U-tube sampler consists of a loop of tubing that forms a U with its terminations at the surface. Beneath the apex of the U-tube, a check valve allows an inlet of formation fluid through a filtered screen. By applying gas pressure at one of the U-legs (driving leg), the check valve can be closed, if the pressure exceeds the hydrostatic pressure of the formation. The loop can be filled with the reservoir fluid by releasing the pressure and opening the check valve, allowing the fluid to rise within the tubing until it reaches the hydrostatic level of the formation. Subsequently, a supply of inert gas under high pressure to the driving leg will close the check valve again and push the fluid out of the sample leg. The amount of sampled fluid depends on the depth and diameter of the tubing [18]. The system is able to keep fluid samples at original reservoir pressures and minimizes gas losses during sampling. It also excludes oxygen contamination from the atmosphere and degassing of dissolved CO_2 from the aqueous fluid, which may lead to rapid changes in sample chemistry and isotope ratios, especially $\delta^{13}C$ DIC of the formation fluid [18, 6]. Together with other down-hole and surface sampling techniques, baseline, injection and post-injection monitoring amounted to 100 gas and fluid samples during the experiment [6]. The CO_2 injection was accomplished in 10 days. Within this period, 41 liquid and more than 15 gas samples were obtained and analyzed for their chemical and isotopic compositions [18]. In addition, a quadrupole mass spectrometer was applied to detect tracer gases including perfluorcarbon (PFT`s), noble gases (Kr, Xe) and SF_6 that were co-injected with the CO_2 stream [17]. Isotope baseline values were reported for $\delta^{13}C$ of DIC, as well as $\delta^{18}O$ of H_2O and injected CO_2 (Tab. 1) [14]. Carbon isotope ratios of DIC and oxygen isotopes of the reservoir brine measured during and after CO_2 injection revealed a clear shift of fluid and gas samples towards $\delta^{13}C$ and $\delta^{18}O$ values of the injected CO_2 (Tab. 1). Therefore, the isotope data was used to trace the dissolution of CO_2 and its conversion into DIC. Oxygen isotope measurements on CO_2 and reservoir fluids also helped to quantify saturation of the sandstone formation with the free CO_2-phase (Tab. 2). Furthermore, isotope analyses revealed the migration of CO_2 into higher stratigraphic sections of the reservoir [14, 17].

2.3 The Pembina Cardium Pilot Study

The Pembina Cardium CO_2 monitoring pilot site in Alberta, Canada offered new possibilities to carry out stable isotope monitoring during an EOR pilot project [19]. In this project, approximately 75,000 tonnes of CO_2 were injected between 2005 and 2008 into a siliciclastic reservoir at a depth of 1650 m below the ground surface. Injection was accomplished by two injection wells that were surrounded by six observation wells [12]. The process started with the injection of supercritical CO_2 as the only phase and changed to an alternating water-gas-regime after two years of injection [19]. After establishing the baseline values of the reservoir and the injected CO_2, a three-year monitoring program was established, with monthly monitoring campaigns [12]. Fluid and gas-samples were collected at the wellheads of the observation wells. Analyses comprised measurements of the isotope composition of CO_2, DIC and water (Tab. 1). Oxygen isotope measurements on H_2O were conducted to estimate the pore-space saturation with free phase CO_2 (Tab. 2) [13]. This approach relies on the expected oxygen isotope equilibration between H_2O and CO_2 [20, 13]. The presence of large amounts of supercritical CO_2 may change the oxygen isotope ratios of the reservoir water if the $\delta^{18}O$ value of the injected CO_2 is distinct from that of the water. The successful application of this method was demonstrated in this project, although previous water flooding of the reservoir complicated the distribution of $\delta^{18}O$ values at the study site [13].

Further studies at the Pembina Cardium site focussed on carbon isotope measurements of CO_2 in casing gas [12] combining $\delta^{13}C$ analyses with CO_2 flux measurements at several observation wells. This combination was used to reveal the proportions of injected CO_2 from gas fluxes at producing wells, as baseline $\delta^{13}C$ values of injected CO_2 had a $\delta^{13}C$ value of about -4.6 ‰. This was more than 10 ‰ higher than the casing gas values before injection (Tab. 1) [12]. Mass balance calculations were used to establish mixing models of residual casing gas with injected CO_2 (Tab. 2). The obtained values matched well with the measured elevated CO_2 concentrations within the wellbore with elevated $\delta^{13}C$ values and indicated the production of injected CO_2 at the sampled wells. This revealed preferential migration of the injected CO_2 along intra-reservoir fractures following a local main stress regime. Wells that were located along these pathways showed the highest CO_2 fluxes with the most elevated $\delta^{13}C$ values [12].

2.4 The Cranefield Experiment

Isotope investigations have also been conducted at the EOR site in Cranfield, Mississippi, USA [11]. The reservoir investigated in this study consists of a depleted oil and gas field with fluvial sandstone- and conglomerate units. Production was abandoned in the 1960´s and the reservoir was not affected by extensive water flooding after this time. Therefore, the site was considered suitable for geochemical monitoring because the reservoir properties were anticipated to have re-equilibrated within this timespan [11]. In 2008, EOR operations began with extensive CO_2 flooding. Until 2011, 2.5 million tonnes of supercritical CO_2 were injected into the reservoir via 24 injection wells at depths of 3050 m. The CO_2 was transported via a pipeline from a nearby natural reservoir with an average $\delta^{13}C$ value of -2.6 ‰ (Tab. 1) [11]. Baseline acquisition was accomplished by the collection of brines from boreholes before the injection started. Sampling campaigns covered a time span of 21 months, during which gas and fluid samples were collected at the wellheads of producing wells [11]. In 2009, the acquisition of the samples was expanded due to the addition of two observation wells that were equipped with U-tube samplers. With this setup 11 brine and 830 gas samples were collected within one month.

Baseline samples revealed that CO_2 was dissolved in the reservoir brine displaying $\delta^{13}C$ values of –8 to –10 ‰ with concentrations ranging from 1 to 5 mole % of dissolved gas in the brine. After commencement of the CO_2 injection, gas produced at monitored wells revealed higher CO_2 concentrations accompanied with enriched $\delta^{13}C$ values compared to baseline values. Isotope mass-balances established plausible mixing models of the injected end-members that matched well with field observations (Tab. 2) [11].

2.5 The Otway Project

At the CO_2CRC Otway project in Australia more than 65.000 tonnes of a CO_2-CH_4 mixture were injected into a depleted natural gas-field. The injection site is located 25 km northwest of Port Campbell, Victoria. After CO_2 injection commenced in March 2008, 124 tonnes of CO_2 were injected per day over a time period of 17 months [21]. The injected gas was taken from CO_2-rich suspended exploratory well and piped 2.25 km to a newly drilled injection well. CO_2 was injected into a saline sandstone aquifer at a depth of about 2000 m [4]. Natural and noble gas tracers were used to verify CO_2 injection in order to detect the breakthrough of the CO_2 plume [4]. Sampling was conducted with a modified U-tube sampling system that comprised check valves at three different levels [21]. Gas samples were collected from the uppermost U-tube, situated inside the gas cap of the reservoir, whereas fluid samples of the formation brine were collected from the two lower levels [4]. Gas samples from the gas cap were lifted up in the U-tube by formation pressure whereas pressurized nitrogen was applied to lift water samples from the two lower reservoir levels. Carbon isotope ratios of produced gas samples as well as degassed CO_2 gained from reservoir brines were analyzed and compared [4]. The injected CO_2 was depleted in ^{13}C by 4.5 ‰ when compared to residual reservoir gas (Tab. 1). This difference was applied as a natural tracer for CO_2 detection that coincided with increases of molar amounts of CO_2 in produced gas samples at the observation well 150 days after the start of injection [4]. Isotope mass balance equations were set up to calculate the amount of isotopically distinct CO_2 that would be required to cause the observed isotope shifts at the observation wells (Tab. 2). Mass balances also helped to determine the proportion of injected and residual CO_2 within the wellbore (Tab. 2) [4]. In this project close to 100 samples were analyzed for their carbon stable isotope ratios.

Table 1 Overview of isotope measurements conducted at selected pilot sites for CCS

Site & Location	t of CO_2 injected [kt]	Isotope system monitored	Number of samples presented	Sampling method	Average isotope value CO_2 injected [$\delta^{13}C$ in ‰ V-PDB $\delta^{18}O$ in ‰ V-SMOW]	Averge isotope value before injection (DIC, CO_2, H_2O) [$\delta^{13}C$ in ‰ V-PDB $\delta^{18}O$ in ‰ V-SMOW]	Average isotope value after injection (DIC, CO_2, H_2O) [$\delta^{13}C$ in ‰ V-PDB $\delta^{18}O$ in ‰ V-SMOW]	References
Weyburn, Saskatchewan, Canada	150600	$\delta^{13}C_{CO2}$; $\delta^{13}C_{HCO3-}$	116 water and gas samples	Well head sampling	$\delta^{13}C$ CO_2 :-20.4	$\delta^{13}C$ CO_2: -16 to -22 $\delta^{13}C$ DIC: -0.4 to -6.6	$\delta^{13}C$ CO_2: -9 to -17 $\delta^{13}C$ DIC: -11.2 to -15.5	[2] [10]
Frio pilot site, Texas, USA	1.6	$\delta^{13}C_{CO2}$; $\delta^{13}C_{HCO3-}$ $\delta^{18}{}_{H2O}$ δD_{H2O}	40 water samples with at least 15 gas samples	Gas samples at Well head; Fluid samples at U-tube f	$\delta^{13}C$ CO_2 : 34 to -44	$\delta^{13}C$ DIC - 5 $\delta^{18}O$ H_2O: 0.8 $\delta^{13}O$ CO_2: 9	$\delta^{13}C$ DIC - 33 $\delta^{18}O$ H_2O: -11.1 $\delta^{13}O$ CO_2: -43	[14] [6]
Pembina Cardium monitoring site Alberta, Canada	75	$\delta^{13}C_{CO2}$ $\delta^{18}O_{CO2}$ $\delta^{13}C_{HCO3-}$ $\delta^{18}{}_{H2O}$ δD_{H2O}	More than 135 gas samples More than 151 fluid samples	Gas and water samples at well head	$\delta^{13}C$ CO_2 : -4.6 $\delta^{13}C$ CO_2 : -28.6	$\delta^{13}C$ CO_2: -16.4 to -23.5 $\delta^{18}O$ H_2O: -14.5 to -17.1	$\delta^{13}C$ CO_2: -5 to -12.3 $\delta^{18}O$ H_2O: -13.7 to -14.7	[13] [12]
Cranfield CO_2 sequestration site, Mississippi, USA	2500	$\delta^{13}C_{CO2}$	More than 850 gas samples More than 35 fluid samples fluid	Gas and water samples at well head, as well as U-tube and downhole sampler	$\delta^{13}C$ CO_2 : -2.6	$\delta^{13}C$ CO_2: -10.5	$\delta^{13}C$ CO_2: -3	[11]
CO2CRC Otway project, Victoria, Australia	65	$\delta^{13}C$ CO_2	About 100 gas samples	U-tube	$\delta^{13}C$ CO_2 : -6.5	$\delta^{13}C$ CO_2: -11.5	$\delta^{13}C$ CO_2: -6.5	[4]
Ketzin pilot site, Germany	65	$\delta^{13}C_{CO2}$ $\delta^{18}O_{CO2}$ $\delta^{13}C_{HCO3-}$	More than 70 fluid samples More than 300 gas samples	Rising tube and GMS for gas samples U-tube and downhole sampler for fluid samples	$\delta^{13}C$ CO_2 : - 3 to - 31	$\delta^{13}C$ DIC: - 4.2 to - 8.4 $\delta^{18}O$ H_2O: -5.5 to - 5.2	$\delta^{13}C$ DIC: - 20 $\delta^{18}O$ H_2O: -5.5 to - 12.0	[22] [24]

Table 2 Overview of isotope mass balances used at various pilot sites for corresponding isotope system; square brackets indicate fractions or concentrations

Site & Location	Purpose / isotope system used	Mass balance equation	Ref.
Frio pilot site, Texas, USA	$\delta^{18}O$ CO_2 and H_2O / saturation with free phase CO_2	$\frac{X_{brine}}{X_{CO2}} = \frac{\delta^{18}O_{inj.\ CO2\ after\ injection} - \delta^{18}O_{inj.\ CO2\ baseline}}{\delta^{18}O_{H2O\ before\ injection} - \delta^{18}O_{H2O\ after\ injection}}$	[14]
Pembina Cardium monitoring site Alberta, Canada	$\delta^{13}C$ CO_2 /proportion of in. CO_2 at produced gas	$\delta^{13}C_{CO2\ measured} = \frac{\delta^{13}C_{CO_2\ injected} \times [CO_{2\ injected}] + \delta^{13}C_{CO_2\ baseline} \times [CO_{2\ baseline\ in\ wellbore}]}{[CO_{2\ measured}]}$ *	[12]
	$\delta^{18}O$ CO_2 and H_2O / fraction of O derived from inj. CO_2	$X^{O}_{derived\ from\ injected\ CO2} = \frac{\delta^{18}O_{H2O\ before\ injection} - \delta^{18}O_{H2O\ after\ injection}}{\delta^{18}O_{H2O\ before\ injection} + \varepsilon - \delta^{18}O_{CO2}}$ **	[13]
Cranfield CO_2 sequestration site, Mississippi, USA	$\delta^{13}C$ CO_2 /mixing between formation CO_2 and CO_2 from injectate	$\delta^{13}C_{sample} =$ $\frac{\delta^{13}C_{formation\ gas} \times [CO_{2\ injectate}] \times [CO_{2\ formation}] - \delta^{13}C_{injectate} \times [CO_{2\ injectate}] \times [CO_{2\ formation}]}{[CO_{2\ injectate}] - [CO_{2\ formation}]} \times \frac{100}{[CO_{2\ sample}]} + \frac{\delta^{13}C_{injectate} \times [CO_{2\ injectate}] - \delta^{13}C_{formation} \times}{[CO_{2\ injectate}] - [CO_{2\ formation}]}$ ***	[11]
CO2CRC Otway project, Victoria, Australia	$\delta^{13}C$ CO_2 / proportion of inj. CO_2 to initial dissolved gas	$\frac{X_{CO2\ injected}}{X_{CO2\ initial\ dissolved}} = \frac{\delta^{13}C_{CO2\ measured} - \delta^{13}C_{CO2\ baseline}}{\delta^{13}C_{CO2\ injected} - \delta^{13}C_{CO2\ baseline}}$	[4]
Ketzin pilot site, Germany	$\delta^{13}C$ DIC / quantifying ionic trapping	$\%DIC\ from\ CO2\ dissolution = \frac{\delta^{13}C_{DIC\ after\ inj.} - \delta^{13}C_{DIC\ baseline}}{\delta^{13}C_{CO2(g)inj.} - \delta^{13}C_{DIC\ baseline}} \times 100$	[24]
	$\delta^{13}C$ CO_2 / proportion of injected CO_2	$\delta^{13}C_{CO2\ measured} = \delta^{13}C_{CO2\ injected} \times \frac{[CO_{2\ injected}]}{[CO_{2\ residual}]} + \delta^{13}C_{baseline} \times \left(1 - \frac{[CO_{2\ injected}]}{[CO_{2\ residual}]}\right)$ ****	

* square brackets indicate fractions of the component where $[CO_{2\ measured}] = 1$

** ε is isotope enrichment factor for CO_2 -water at reservoir temperature

*** square brackets indicate CO_2 content in the gas in %

**** square brackets indicate fractions of the gas component

2.6 The Ketzin Pilot Site

The Ketzin pilot site is the longest operating onshore test injection site for CCS in Europe. Injection of CO_2 began in 2008 into a saline aquifer at approximately 640 m depth below the ground surface. The purpose of this ongoing project was to establish sound scientific knowledge about CO_2 behaviour in the subsurface as well as to test and develop appropriate monitoring strategies [22]. The site has a pre-injection facility with two 50-ton storage tanks, one injection well and two observation wells at 50 and 100 m distance from the injector. A third observation well that reaches the reservoir will be completed by the end of 2012. At first, sampling of reservoir brine was achieved by downhole samplers. Also a newly developed gas membrane sensor (GMS) combined with a portable quadrupole mass-spectrometer allowed in situ and real-time analyses of dissolved gases within the reservoir brine [8]. After the supercritical CO_2 displaced most of the reservoir brine around the observation wells, a rising tube was installed that allowed continuous gas sampling from the reservoir. The rising tube produces about 8 liters of CO_2 per hour, supported by the reservoir pressure [22].

Stable isotope measurements had been_conducted since the beginning of the CO_2 injection in 2008. Investigations started with a detailed geochemical baseline characterization of the reservoir and overlying formations, comprising $\delta^{13}C$ and $\delta^{18}O$ data of brine DIC and H_2O (Tab. 1) [23]. After this baseline characterization, stable carbon isotopes of the dissolved inorganic carbon have been determined to confirm the CO_2 arrival at two observation wells as well as to quantify solubility trapping within the reservoir brine using isotope mass balances (Tab. 2) [24]. In addition, in 2011, a further amount of more than 1500 tons of isotopically different CO_2 from an oxyfuel pilot plant was injected over a time period of approximately 2 months. This CO_2 had a $\delta^{13}C$ value that was 2 ‰ more positive than that of the previously injected CO_2. This caused an isotope shift at one observation well that coincided with the breakthrough of simultaneously injected noble gas tracers [22].

Further CO_2 gas monitoring in the reservoir, including the road tankers that supply the site with CO_2, revealed also that during normal injection processing two isotopically very different kinds of CO_2 were injected. This difference is attributed to the different sources of the CO_2. The first source provides the vast majority of all injected CO_2 and is an oil refinery that produces technical grade CO_2 with an average $\delta^{13}C$ value of about –30 ‰. The other source is a natural CO_2 accumulation that provides CO_2 with a $\delta^{13}C$ value of about -3‰. The isotopically distinct CO_2 from the natural source is injected in smaller amounts and sporadically at time intervals of several days to weeks. Recent studies at Ketzin focus on exploiting these differences in $\delta^{13}C$ values between technical and natural source CO_2, which amount to a maximum of 28 ‰ (Tab. 1). Different isotope compositions generated from the sporadic charging with isotopically distinct natural source CO_2 into the pre-injection tanks can be characterized before injection and should subsequently be identified at an observation well. If so, this would provide an excellent additional tracer because the isotopically distinct CO_2

from the natural source that has been injected alternately since beginning of injection provides an opportunity to validate migration models by using isotope mass balances (Tab. 2).

In Addition to the gas tracer experiments, isotope investigations are applied in order to support leakage detection of the above reservoir zone. In 2011, an observation well was completed within the closest stratigraphic overlying aquifer [22]. The well contains several down-hole geophysical devices as well as a U-tube sampler. It is part of a new monitoring concept, which aims at detecting potential leakage of the first barrier as soon as possible [25]. Within this concept, frequent stable isotopes monitoring of the formation brine DIC is a substantial part. Leaking CO_2 from the reservoir is assumed to be detectable with the aid of stable carbon isotopes, because it would change the $\delta^{13}C$ value of the DIC in a systematic manner [25].

Analytical and sampling methods were continuously improved at Ketzin. Modifying a traditional isotope ratio mass spectrometer and its autosampler with additional He-dilution allows determination of samples with up to 100 % CO_2 content without further pre-dilution in the laboratory. In addition, sampling in the field was simplified by flushing standard laboratory sampling vials with 100 % CO_2 gas samples that are subsequently analyzed in the laboratory. This enabled isotope measurements of more than 260 samples within a time period of three months. Overall, 74 fluid samples and 310 gas samples were analyzed for their carbon and oxygen isotopic signature within the project period at Ketzin.

3 Conclusions

While a number of ongoing and recently started projects were not considered in this paper, this review has shown that, worldwide, a total of more than 1000 isotope measurements were carried out during CO_2 storage projects for various purposes. The main use of these measurements is to improve the understanding of gas - water - rock interaction under elevated pressure and temperature conditions, CO_2 migration in the subsurface as well as leakage detection.

This review demonstrates that stable isotope monitoring represents an important tool in CO_2 storage and enhanced hydrocarbon recovery projects. This technique requires detailed planning of sampling strategies and needs to account for degassing of fluids before sampling. Therefore, down-hole sampling techniques such as the U-tube system or rising tubes for gas samples should be preferred. However, as has been shown, data obtained from wellhead sampling can also provide sufficiently accurate information, when corrections for geochemical alteration are applied. This seems especially important for isotope applications in large scale CCS or commercial EOR/EGR projects, because they usually comprise of numerous injection, production and/or observation wells, which can not be equipped with complex down hole sampling tools as it is usually done at smaller scale pilot sites. However, there is a lack of detailed studies that compare isotope measurements from wellhead sampling with down-hole techniques.

Like many other monitoring methods, isotope studies also require detailed baseline monitoring before CO_2 injection starts in order to facilitate comparisons of geochemical changes. Furthermore, sufficient baseline data of reservoir isotope ($\delta^{13}C$, $\delta^{18}O$) and concentration values, injection rates and isotope measurements during and after injection allow the application of highly useful isotope mass balances. The latter are the most commonly applied techniques in stable isotope utilizations. They allow quantifications of several key-processes accompanying CO_2 injection into the subsurface including ionic trapping, plume development and CO_2 migration.

The above stable isotope techniques are limited by low spatial resolution, caused by a sparse number of observation wells. This is also often combined by insufficient temporal resolution with too low sampling frequencies. However, new developments in mass spectrometry with new generation mobile laser-based instruments are promising. They simplify measurements of $\delta^{13}C$ and $\delta^{18}O$ in both, gases and fluids. These new sensors are applicable in the field and allow on-line measurements. With this, stable isotope measurements can become an increasingly applied method and a substantial part of complementary monitoring systems for CCS.

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References

1. Freifeld, B.M., Daley, T.M., Hovorka, S.D., Henninges, J., Underschultz, J., Sharma, S.: Recent advances in well-based monitoring of CO_2 sequestration. Energy Procedia 1(1), 2277–2284 (2009)
2. Emberley, S., Hutcheon, I., Shevalier, M., Durocher, K., Mayer, B., Gunter, W.D., Perkins, E.H.: Monitoring of fluid-rock interaction and CO_2 storage through produced fluid sampling at the Weyburn CO_2-injection enhanced oil recovery site, Saskatchewan, Canada. Appl. Geochem. 20(6), 1131–1157 (2005), doi:10.1016/J.Apgeochem.2005.02.007
3. Kharaka, Y.K., Cole, D.R., Thordsen, J.J., Kakouros, E., Nance, H.S.: Gas-water-rock interactions in sedimentary basins: CO_2 sequestration in the Frio Formation, Texas, USA. J. Geochem. Explor. 89(1-3), 183–186 (2006), doi:10.1016/J.Gexplo.2005.11.077
4. Boreham, C., Underschultz, J., Stalker, L., Kirste, D., Freifeld, B., Jenkins, C., Ennis-King, J.: Monitoring of CO_2 storage in a depleted natural gas reservoir: Gas geochemistry from the CO2CRC Otway Project, Australia. Int. J. Greenh. Gas Con. 5(4), 1039–1054 (2011), doi:10.1016/J.Ijggc.2011.03.011
5. Emberley, S., Hutcheon, I., Shevalier, M., Durocher, K., Gunter, W.D., Perkins, E.H.: Geochemical monitoring of fluid-rock interaction and CO_2 storage at the Weyburn CO2-injection enhanced oil recovery site, Saskatchewan, Canada. Energy 29(9-10), 1393–1401 (2004), doi:10.1016/J.Energy.2004.03.073

6. Kharaka, Y.K., Thordsen, J.J., Hovorka, S.D., Nance, H.S., Cole, D.R., Phelps, T.J., Knauss, K.G.: Potential environmental issues of CO2 storage in deep saline aquifers: Geochemical results from the Frio-I Brine Pilot test, Texas, USA. Appl. Geochem. 24(6), 1106–1112 (2009), doi:10.1016/J.Apgeochem.2009.02.010
7. Shi, J.Q., Sinayuc, C., Durucan, S., Korre, A.: Assessment of carbon dioxide plume behaviour within the storage reservoir and the lower caprock around the KB-502 injection well at In Salah. Int. J. Greenh. Gas Con. 7, 115–126 (2012), doi:10.1016/J.Ijggc.2012.01.002
8. Zimmer, M., Erzinger, J., Kujawa, C.: The gas membrane sensor (GMS): A new method for gas measurements in deep boreholes applied at the CO2SINK site. Int. J. Greenh. Gas Con. 5(4), 995–1001 (2011)
9. Ghosh, P., Brand, W.A.: Stable isotope ratio mass spectrometry in global climate change research. International Journal of Mass Spectrometry 228(1), 1–33 (2003)
10. Raistrick, M., Mayer, B., Shevalier, M., Perez, R.J., Hutcheon, I., Perkins, E., Gunter, B.: Using chemical and isotopic data to quantify ionic trapping of injected carbon dioxide in oil field brines. Environ. Sci. Technol. 40(21), 6744–6749 (2006), doi:10.1021/Es060551a
11. Lu, J.M., Kharaka, Y.K., Thordsen, J.J., Horita, J., Karamalidis, A., Griffith, C., Hakala, J.A., Ambats, G., Cole, D.R., Phelps, T.J., Manning, M.A., Cook, P.J., Hovorka, S.D.: CO_2-rock-brine interactions in Lower Tuscaloosa Formation at Cranfield CO_2 sequestration site, Mississippi, USA. Chem. Geol. 291, 269–277 (2012), doi:10.1016/J.Chemgeo.2011.10.020
12. Johnson, G., Mayer, B., Shevalier, M., Nightingale, M., Hutcheon, I.: Tracing the movement of CO2 injected into a mature oilfield using carbon isotope abundance ratios: The example of the Pembina Cardium CO_2 Monitoring project. Int. J. Greenh. Gas Con. 5(4), 933–941 (2011), doi:10.1016/J.Ijggc.2011.02.003
13. Johnson, G., Mayer, B., Nightingale, M., Shevalier, M., Hutcheon, I.: Using oxygen isotope ratios to quantitatively assess trapping mechanisms during CO_2 injection into geological reservoirs: The Pembina case study. Chem. Geol. 283(3-4), 185–193 (2011), doi:10.1016/J.Chemgeo.2011.01.016
14. Kharaka, Y.K., Cole, D.R., Hovorka, S.D., Gunter, W.D., Knauss, K.G., Freifeld, B.M.: Gas-water-rock interactions in Frio Formation following CO_2 injection: Implications for the storage of greenhouse gases in sedimentary basins. Geology 34(7), 577–580 (2006), doi:10.1130/G22357.1
15. Mayer, B., Shevalier, M., Nightingale, M., Kwon, J.S., Johnson, G., Raistrick, M., Hutcheon, I., Perkins, E.: Tracing the movement and the fate of injected CO_2 at the IEA GHG Weyburn-Midale CO_2 monitoring and storage project (Saskatchewan, Canada) using carbon isotope ratios. Int. J. Greenh. Gas Con. (submitted)
16. Shevalier, M., Durocher, K., Perez, R.J., Hutcheon, I., Mayer, B., Perkins, E., Gunter, B.: Geochemical monitoring of gas-water-rock interaction at the iea Weyburn CO_2 Monitoring and Storage Project, Saskatchewan, Canada. In: Rubin, E.S., Keith, D.W., Gilboy, C.F., et al. (eds.) Greenhouse Gas Control Technologies 7, pp. 2135–2139. Elsevier Science Ltd., Oxford (2005)
17. Hovorka, S.D., Benson, S.M., Doughty, C., Freifeld, B.M., Sakurai, S., Daley, T.M., Kharaka, Y.K., Holtz, M.H., Trautz, R.C., Nance, H.S., Myer, L.R., Knauss, K.G.: Measuring permanence of CO_2 storage in saline formations: The Frio experiment. Environmental Geosciences 13(2), 105–121 (2006)

18. Freifeld, B.M., Trautz, R.C., Kharaka, Y.K., Phelps, T.J., Myer, L.R., Hovorka, S.D., Collins, D.J.: The U-tube: A novel system for acquiring borehole fluid samples from a deep geologic CO_2 sequestration experiment. J. Geophys. Res.-Sol. Ea. 110(B10) (2005), doi:Artn B10203
19. Shevalier, M., Nightingale, M., Johnson, G., Mayer, B., Perkins, E., Hutcheon, I.: Monitoring the reservoir geochemistry of the Pembina Cardium CO_2 monitoring project, Drayton Valley, Alberta. Energy Procedia 1(1), 2095–2102
20. Vogel, J.C., Grootes, P.M., Mook, W.G.: Isotopic fractionation between gaseous and dissolved carbon dioxide. Zeitschrift für Physik 230(3), 225–238 (1970)
21. Stalker, L., Boreham, C., Underschultz, J., Freifeld, B., Perkins, E., Schacht, U., Sharma, S.: Geochemical monitoring at the CO2CRC Otway Project: tracer injection and reservoir fluid acquisition. Energy Procedia 1, 2119–2125 (2009)
22. Martens, S., Kempka, T., Liebscher, A., Lüth, S., Möller, F., Myrttinen, A., Norden, B., Schmidt-Hattenberger, C., Zimmer, M., Kühn, M.: Europe's longest-operating onshore CO_2 storage site at Ketzin, Germany: a progress report after three years of injection. Environmental Earth Sciences 67(2), 323–334 (2012)
23. Förster, A., Norden, B., Zinck-Jörgensen, K., Frykman, P., Kulenkampff, J., Spangenberg, E., Erzinger, J., Zimmer, M., Kopp, J., Borm, G., Juhlin, C., Cosma, C.G., Hurter, S.: Baseline characterization of the CO2SINK geological storage site at Ketzin, Germany. Environmental Geosciences 13(3), 145–161 (2006)
24. Myrttinen, A., Becker, V., van Geldern, R., Wurdemann, H., Morozova, D., Zimmer, M., Taubald, H., Blum, P., Barth, J.A.C.: Carbon and oxygen isotope indications for CO(2) behaviour after injection: First results from the Ketzin site (Germany). Int. J. Greenh. Gas Con. 4(6), 1000–1006 (2010), doi:10.1016/J.Ijggc.2010.02.005
25. Wiese, B., Zimmer, M., Nowak, M., Pilz, P.: Above-zone well-based hydraulic and geochemical monitoring of the CO_2 reservoir in Ketzin, Germany. Environmental Earth Sciences (Special Issue Geoenergy) (2012) (submitted)