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The use of stable isotope measurements for monitoring and verification of CO₂ storage

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Abstract

Stable isotope data can assist in successful monitoring of the fate of injected CO₂ in enhanced oil recovery and geological storage projects. This is demonstrated for the International Energy Agency Greenhouse Gas Weyburn-Midale CO₂ Monitoring and Storage Project (Saskatchewan) and the Pembina Cardium CO₂ Monitoring Project (Alberta) where fluid and gas samples from multiple wells were collected and analyzed for geochemical and isotopic compositions. In both projects, C and O isotope values of injected CO₂ were sufficiently distinct from those of background CO₂ in the reservoir. Consequently C and O isotope ratios constitute a suitable ‘fingerprint’ for tracing the fate of injected CO₂ in the respective reservoirs.

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1. Introduction

Global atmospheric concentrations of carbon dioxide (CO₂) have increased markedly as a result of human activities since 1750 and now far exceed pre-industrial values determined from ice cores spanning several hundred thousands of years [1]. The recent global increase in atmospheric carbon dioxide concentration is due primarily to fossil fuel combustion [2]. At the current rate of increase in atmospheric CO₂ concentrations (~2ppm/year) further warming and changes in the global climate system will very likely be larger than those already observed during the 20th century [2]. It is thus likely that anthropogenic CO₂ emissions must be reduced to stabilize the climate “to preserve a planet on which civilization developed and to which life on Earth is adapted” [3].

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Carbon Capture and Storage (CCS) is a promising component of any serious plan to reduce anthropogenic CO₂ emissions to the atmosphere and thereby mitigate future impacts of human-induced climate change [4]. CCS associated with the combustion of fossil fuels allows for near carbon neutrality (typically capture is 90% of CO₂ emissions) whilst still exploiting the energy gain from carbon based fuels. A successful CCS project must demonstrate that the injected CO₂ is safely and securely sequestered in the chosen reservoir. Combined geophysical and geochemical monitoring programs have the potential to determine the fate of the injected CO₂ in the reservoir and to assess the nature and effectiveness of the storage mechanisms [5].

As CO₂ is injected into reservoirs it will undergo a number of physical and chemical reactions [6]. CO₂ density will increase with increasing depth and when the CO₂ reaches its critical point (31°C and 74bar) at depths of approximately 800m [7] in the subsurface it will become a supercritical fluid. Interaction between the CO₂ and the reservoir fluids will lead to a variety of dissolution processes and partitioning of the CO₂ into different phases. A portion of the CO₂ will stay as free phase supercritical fluid, some will dissolve in residual hydrocarbons in the reservoir and some will dissolve in the reservoir fluids. In the latter case CO₂ will undergo a number of chemical reactions that include the following [8,9]:



After commencement of CO₂ injection, geochemical patterns in reservoir fluids and gases will reveal the above-mentioned processes. For example, the production of hydrogen ions (equation 2) will decrease pH while the bicarbonate ions produced in the same equation will increase alkalinity when the hydrogen ions are buffered by water-rock reactions. Geochemical data obtained for reservoir fluids and gases can therefore be used to monitor the fate of CO₂ in the subsurface. This is particularly true if injected CO₂ can be distinguished from carbon compounds in the reservoir by tracer techniques. Stable isotope ratios of carbon and oxygen (expressed as δ¹³C and δ¹⁸O values) can be easily determined for injected CO₂ and carbon compounds in reservoir fluids and gases by a suitable geochemical monitoring and measurement program. It is essential to determine the isotopic composition of CO₂ (and DIC) in the reservoir prior to CO₂ injection. If the injected CO₂ is isotopically distinct with respect to baseline CO₂, stable isotope ratios can be used as ‘fingerprints’ and facilitate monitoring of the migration and behavior of the CO₂ in the reservoir after commencement of CO₂ injection. The objective of this paper is to demonstrate the usefulness of isotopic tracers for geochemical monitoring of injected CO₂.

2. Study areas

Data from two CO₂-Enhanced Oil Recovery (EOR) projects in western Canada are used to demonstrate the feasibility of using geochemical and isotopic data to trace the fate of injected CO₂ in the subsurface. The sites are the International Energy Agency Greenhouse Gas Weyburn - Midale CO₂ Monitoring and Storage Project in southern Saskatchewan and the Pembina Cardium CO₂ Monitoring Project in central Alberta (Fig. 1). The Mississippian Midale beds of the carbonate reservoir at Weyburn consist of an upper dolostone ‘Marly’ unit and a lower limestone ‘Vuggy’ unit into which CO₂ has been injected since 2000 [10]. In contrast, CO₂ at the Pembina project is injected into the siliciclastic Upper Cretaceous Cardium formation that comprises a series of stacked sandstone reservoirs (see companion paper by Nightingale et al. for full mineralogy). This provides an excellent opportunity to study and compare the interaction of CO₂ with two contrasting sedimentary reservoir lithologies: siliciclastics and carbonates.

3. Methods

To monitor changes in the CO₂ distribution in the reservoir, the geochemical and isotopic composition of the fluids and gases must be determined at regular intervals throughout the duration of the project. One critical aspect is the establishment of a baseline pre-injection study. The baseline study will reveal both the ‘natural’ state of the reservoir fluids before CO₂ injection and should also aim at elucidating natural variability in the reservoir.

Sample collection differs slightly at the two sites due to the operation of the reservoir and chemical composition of the fluids (e.g. high H₂S values at Weyburn), however generalities can be drawn. Emberley et al. [11] described

the procedures in detail, that, in summary, are the collection of multiple gas, oil and water samples at each well monitored in the project and the subsequent analyses. At Pembina 8 wells were sampled and at Weyburn 43 were sampled. Analysis of the fluid and gas samples revealed up to 40 individual parameters for each well on each of 3 baseline and 28 monitoring trips at Pembina and 1 baseline and 10 monitor trips at Weyburn. These included: alkalinity, pH, gas composition (CO_2 , H_2S , C1-4), major ionic species (Na, K, Cl, Ca, Mg, Fe etc) and C, O and S isotopic compositions of various compounds.

CO_2 in the casing gas from the wells was collected in sealed containers and the chemical composition was analyzed in the field using a Varian CP4900 Micro GC. In the laboratory, the samples were analyzed for carbon isotope ratios of CO_2 ($\delta^{13}\text{C}_{\text{CO}_2}$) using a GC coupled to an isotope ratio mass spectrometer (IRMS). $\delta^{13}\text{C}$ values are recorded in per mil (‰) relative to V-PDB. Accuracy and precision for the $\delta^{13}\text{C}_{\text{CO}_2}$ values is better than ± 0.5 ‰. Oxygen isotope ratios of CO_2 ($\delta^{18}\text{O}_{\text{CO}_2}$) were also determined by comparison against oxygen isotope ratios of CO_2 generated from internationally accepted reference materials and are reported versus V-SMOW. Samples for oxygen isotope ratio determinations on reservoir fluids were collected in 15 mL plastic vacu-tubes and $\delta^{18}\text{O}$ values were determined by using equilibration techniques coupled with dual inlet IRMS. Oxygen isotope ratios are recorded using the usual delta (δ) notation ($\delta^{18}\text{O}_{\text{H}_2\text{O}}$) in per mil (‰) deviation relative to V-SMOW with an analytical uncertainty of $< \pm 0.2$ ‰.

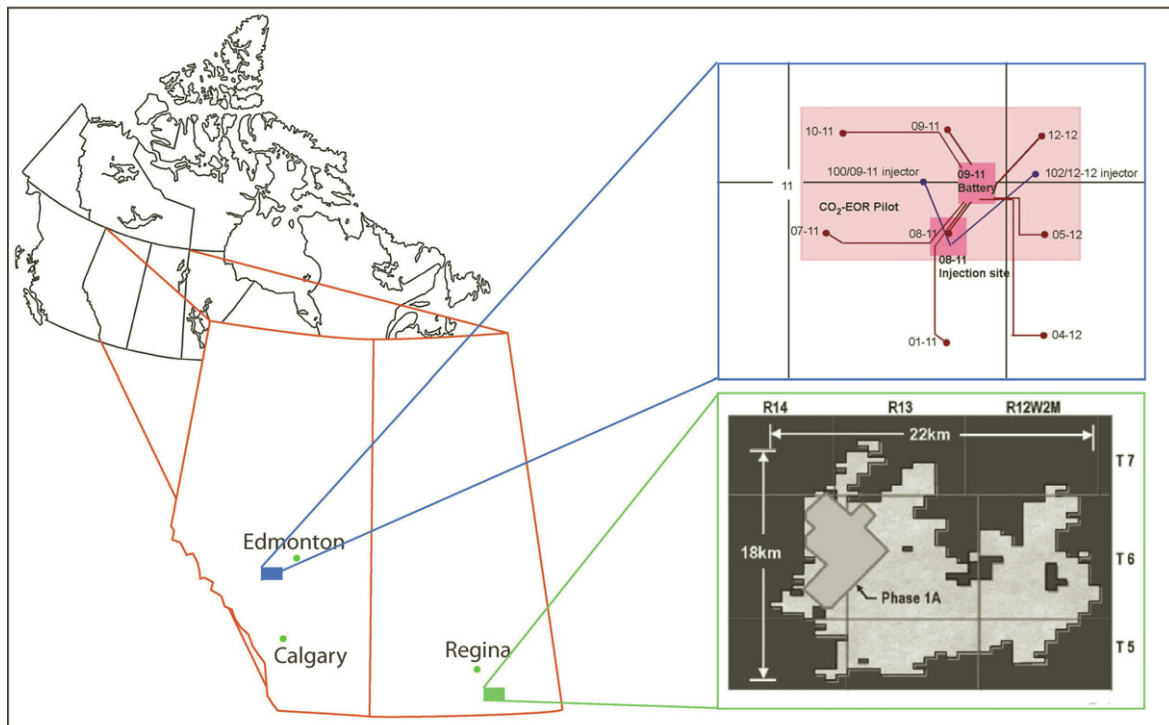


Figure 1: Locations of study sites in western Canada. Blue box Pembina Cardium CO_2 Monitoring Project. Green Box: International Energy Agency Greenhouse Gas Weyburn-Midale CO_2 Monitoring and Storage Project.

4. Results

CO_2 contents (in mole %) and $\delta^{13}\text{C}$ of CO_2 and $\delta^{18}\text{O}$ of H_2O values were determined for both projects and are displayed for selected observation wells in Figures 2 and 3.

4.1. Carbon isotope ratios

Figure 2 shows both the mole % CO₂ and the $\delta^{13}\text{C}_{\text{CO}_2}$ values against time lapsed in the monitoring project for two selected wells at Weyburn. Baseline $\delta^{13}\text{C}$ values of CO₂ gas ($\delta^{13}\text{C}_{\text{CO}_2}$) were between -12‰ and -14‰ while baseline CO₂ concentrations were < 10 mole %. The injected CO₂ at Weyburn comes from a coal gasification plant in North Dakota and has a $\delta^{13}\text{C}_{\text{CO}_2}$ value of -20.4 ‰. After CO₂ injection commenced, geochemical data for Well 1 revealed that CO₂ contents increased to reach values of 70-90 mole % (Fig. 2a) after over a year of injection whilst $\delta^{13}\text{C}_{\text{CO}_2}$ values steadily decreased to values near -20 ‰ (Fig. 2b). In contrast, geochemical data for Well 2 displayed only a minor increase in CO₂ concentration with time (Fig. 2d) while the $\delta^{13}\text{C}_{\text{CO}_2}$ values trended towards values near -20 ‰ circa one year after CO₂ injection began (Fig. 2e).

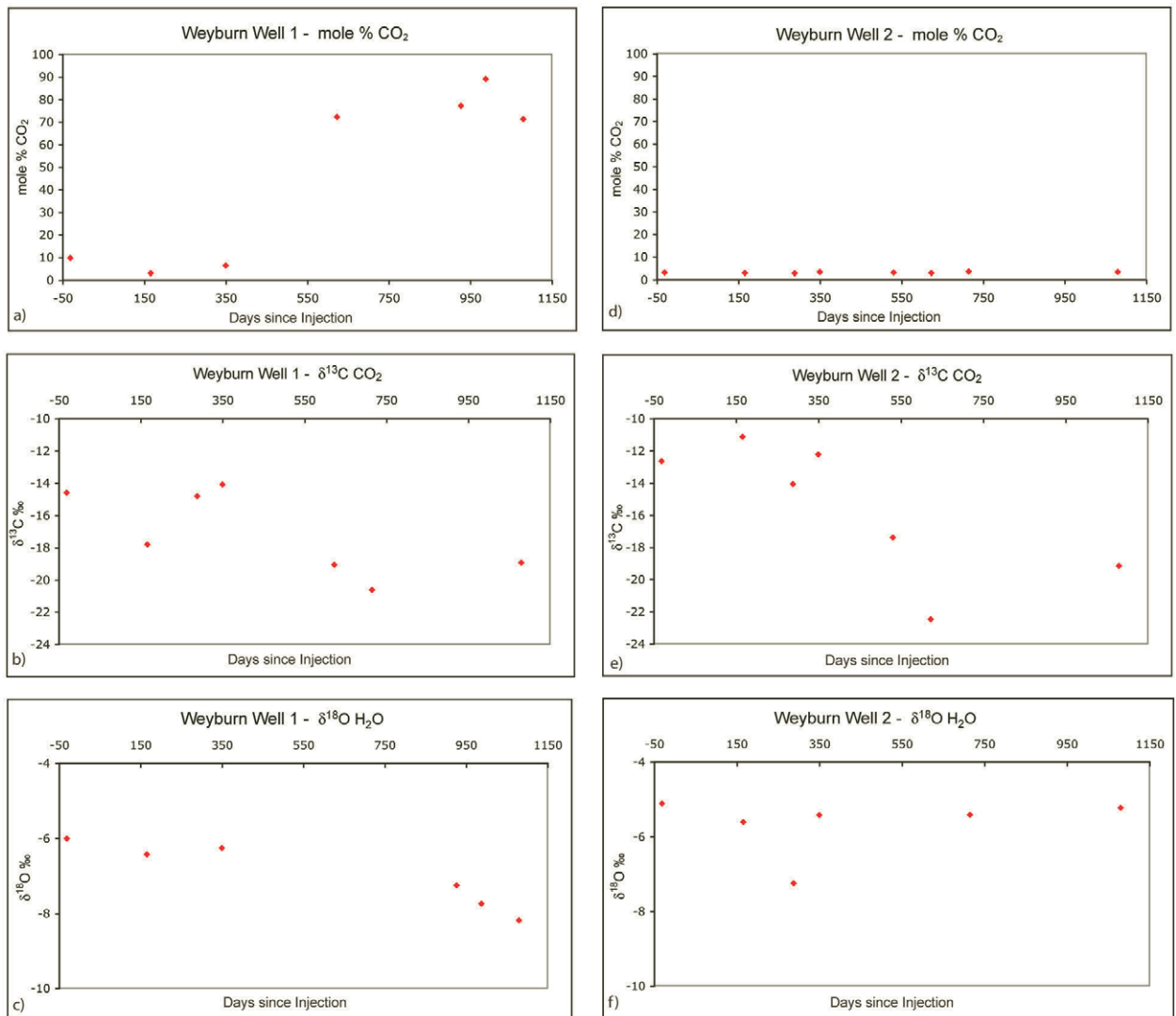


Figure 2: Weyburn isotope ratios. a) Mole % CO₂ vs. Days since Injection, Weyburn Well 1. b) $\delta^{13}\text{C}_{\text{CO}_2}$ vs. Days since Injection, Weyburn Well 1. c) $\delta^{18}\text{O}_{\text{H}_2\text{O}}$ vs. Days since Injection, Weyburn Well 1. d) Mole % CO₂ vs. Days since Injection, Weyburn Well 2. e) $\delta^{13}\text{C}_{\text{CO}_2}$ vs. Days since Injection, Weyburn Well 2. f) $\delta^{18}\text{O}_{\text{H}_2\text{O}}$ vs. Days since Injection, Weyburn Well 2.

Figure 3 summarizes both the mole % CO₂ and the $\delta^{13}\text{C}_{\text{CO}_2}$ values against time lapsed in the monitoring project for two selected wells at Pembina. Baseline $\delta^{13}\text{C}$ values for CO₂ gas were between -16 ‰ and -18 ‰ and CO₂

concentrations at baseline were ~ 1 mole %. CO₂ injected at Pembina is trucked in daily and has a mean $\delta^{13}\text{C}$ value of -4.5 ± 2 ‰ depending on the source of the CO₂. Geochemical data for Well 1 revealed that CO₂ concentrations increased rapidly as CO₂ injection began to maximum values around 90% (Fig. 3a) within 6 months of injection. At the same time $\delta^{13}\text{C}_{\text{CO}_2}$ values increased rapidly towards values of -5 ‰ (Fig. 3b). Geochemical data for Well 2 showed negligible changes in CO₂ concentration with time (Fig. 3d) while $\delta^{13}\text{C}$ values trended towards -8 ‰ over a period of 6 months after injection began (Fig. 3e).

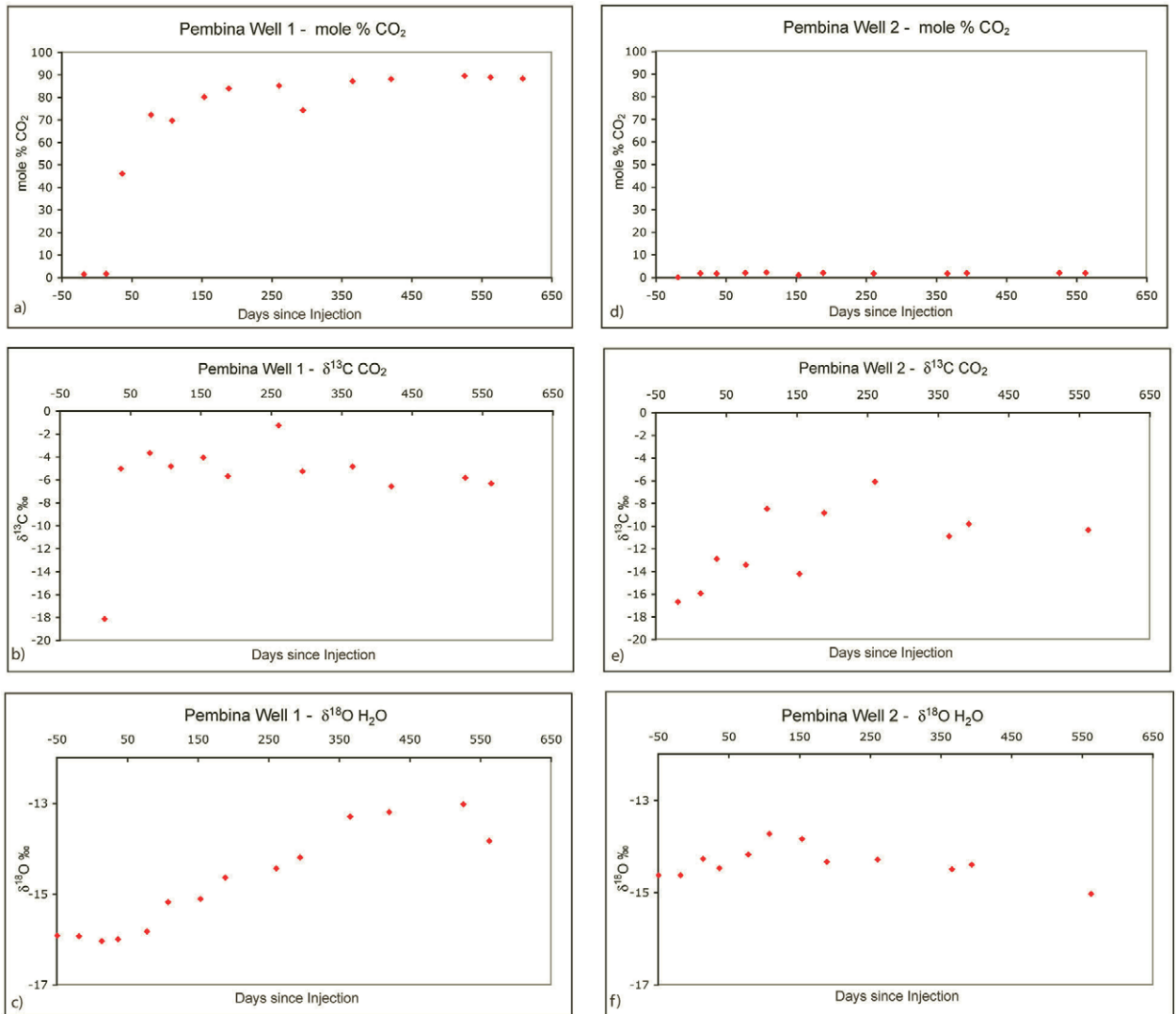


Figure 3: Pembina isotope ratios. a) Mole % CO₂ vs. Days since Injection, Pembina Well 1. b) $\delta^{13}\text{C}_{\text{CO}_2}$ vs. Days since Injection, Pembina Well 1. c) $\delta^{18}\text{O}_{\text{H}_2\text{O}}$ vs. Days since Injection, Pembina Well 1. d) Mole % CO₂ vs. Days since Injection, Pembina Well 2. e) $\delta^{13}\text{C}_{\text{CO}_2}$ vs. Days since Injection, Pembina Well 2. f) $\delta^{18}\text{O}_{\text{H}_2\text{O}}$ vs. Days since Injection, Pembina Well 2.

4.2. Oxygen isotope ratios

Oxygen isotope ratios ($\delta^{18}\text{O}$) of injected CO₂ and of fluids ($\delta^{18}\text{O}_{\text{H}_2\text{O}}$) obtained from the same observation wells described above were determined. Baseline $\delta^{18}\text{O}_{\text{H}_2\text{O}}$ values for brines at Weyburn were ~ -6 ‰. Injected CO₂ had a $\delta^{18}\text{O}$ value of $+4.9$ ‰ vs. V-SMOW. As CO₂ content increased at Well 1 (Fig. 2a) the $\delta^{18}\text{O}_{\text{H}_2\text{O}}$ values of the

reservoir brine decreased by approximately 2 ‰ (Fig. 2c). In contrast, the $\delta^{18}\text{O}$ value of the reservoir brine remained unchanged at ~ -6 ‰ at Well 2 (Fig. 2f) where no significant change in CO_2 concentration was observed (Fig. 2d).

At Pembina the baseline $\delta^{18}\text{O}$ values for the reservoir fluids were -15 to -16 ‰. Injected CO_2 had a $\delta^{18}\text{O}$ value of $+28.7$ ‰ vs. V-SMOW. As CO_2 concentrations increased in Well 1 (Fig. 3a) $\delta^{18}\text{O}_{\text{H}_2\text{O}}$ values increased by ~ 3 ‰ (Fig. 3c). In contrast the $\delta^{18}\text{O}_{\text{H}_2\text{O}}$ values remained unchanged (-15 ‰) in Well 2 (Fig. 3f) that experienced no significant increase in CO_2 contents (Fig. 3d).

5. Discussion

In assessing trends of $\delta^{13}\text{C}_{\text{CO}_2}$, the detection of CO_2 across the spatial extent of the reservoir is addressed. Figures 2 and 3 show that as CO_2 concentrations increase, the $\delta^{13}\text{C}_{\text{CO}_2}$ values trend towards that of the injected CO_2 . Note that this trend away from baseline $\delta^{13}\text{C}$ values towards that of the injected CO_2 , in opposite senses of direction (towards positive or negative), is simply as a result of the Weyburn CO_2 having a more negative isotope signature than the baseline CO_2 , and conversely, the Pembina CO_2 having a more positive $\delta^{13}\text{C}$ value. This trend is indicative of injected CO_2 migrating towards the wells where the CO_2 is sampled.

Well 2 at both Weyburn (Fig. 2d,e) and Pembina (Fig. 3d,e) show that even with very small increases in CO_2 concentration at the wells, the $\delta^{13}\text{C}_{\text{CO}_2}$ values trend toward the value of the injected CO_2 . Figure 4 explains these trends further. The data plotted as crosses on Figure 4 are the data represented in Figures 2 and 3. The solid lines represent the theoretical two endmember mixing curve between background and injected CO_2 . Where initial concentrations of CO_2 are low, as at both wells at Pembina, the addition of small amounts of CO_2 rapidly changes the $\delta^{13}\text{C}$ value of the sample. At 10 mole % CO_2 , more than 90% of the CO_2 will be from the injection source and hence the $\delta^{13}\text{C}$ values approach those of the injected CO_2 . At Weyburn, where initial CO_2 concentrations are markedly higher, additional injected CO_2 will change the carbon isotope value at different rates. At Well 1, with 9% CO_2 at baseline, the carbon isotope response will be slower than at Well 2 (3% CO_2 at baseline) assuming a similar rate of injected CO_2 reaching each well. At the point when injected CO_2 comprises 90% of the sample at Weyburn, mole % CO_2 has to be significantly higher than at Pembina (90 and 40% for Well 1 and 2 respectively). Thus, Figure 4 indicates also that $\delta^{13}\text{C}_{\text{CO}_2}$ can be used as an early identifier of injected CO_2 breakthrough at individual wells. It also indicates that significant attention must be paid to both the distinction between background and injected CO_2 isotope values and to the host lithology (and hence initial CO_2 concentrations in the reservoir) when monitoring CO_2 projects.

The $\delta^{18}\text{O}_{\text{H}_2\text{O}}$ trends reveal the extent to which oxygen in the CO_2 has been exchanged with the oxygen in the reservoir brines. Kharaka et al. [12] showed that in a CO_2 storage setting the volume of CO_2 sourced oxygen in the system can increase to the point where it influences the $\delta^{18}\text{O}$ values of the reservoir fluids. Due to the relatively low abundance of oxygen that could be liberated by water-rock interactions, the only other reaction that could change the value of the $\delta^{18}\text{O}_{\text{H}_2\text{O}}$ would be water injection into the reservoir. Water injection would also change the hydrogen isotope values ($\delta^2\text{H}$). The wells that showed change in $\delta^2\text{H}$ were omitted from this study so that changes in $\delta^{18}\text{O}_{\text{H}_2\text{O}}$ were due to CO_2 interaction only. In Figure 2 and 3 it can be seen that when CO_2 concentration increased significantly the $\delta^{18}\text{O}_{\text{H}_2\text{O}}$ value is influenced whereas when CO_2 concentration does not change significantly the $\delta^{18}\text{O}_{\text{H}_2\text{O}}$ value remains constant. This indicates that in Well 1 at both Weyburn and Pembina there is enough CO_2 in contact with the water to influence its $\delta^{18}\text{O}$ value. Conversely, at Well 2 at both sites there is too little CO_2 to change the $\delta^{18}\text{O}_{\text{H}_2\text{O}}$ value.

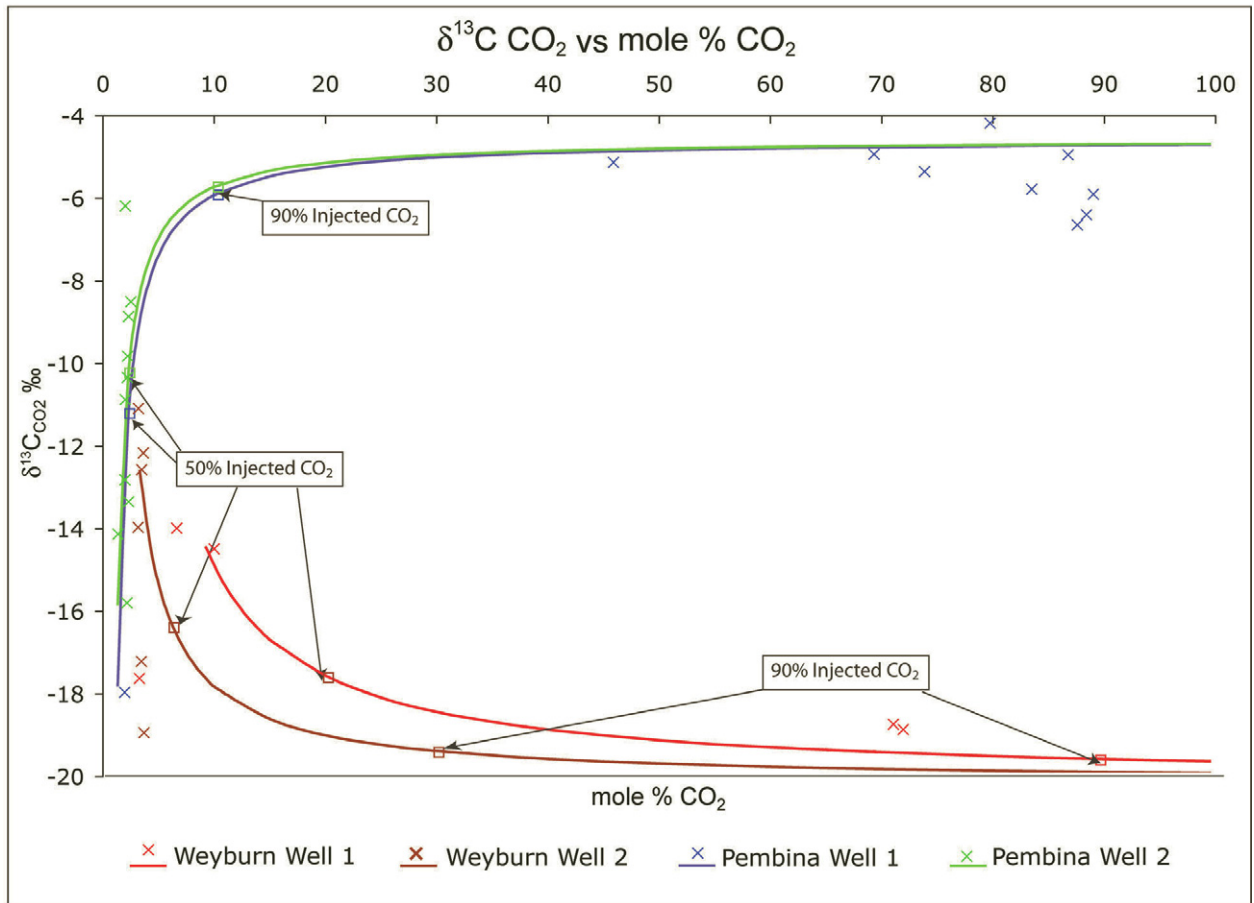


Figure 4. $\delta^{13}\text{C}_{\text{CO}_2}$ versus mole % CO_2 for Wells 1 and 2 at both Weyburn and Pembina. Solid lines show the theoretical two endmember mixing curve between background and injected CO_2 for each well. Crosses represent measurements taken at all four wells. The squares and labels indicate the theoretical points at which injected CO_2 comprises 50% and 90% of the CO_2 sample at each well.

6. Conclusion

Regulatory and safety issues dictate that successful CCS projects will require the ability to trace the fate of CO_2 in the reservoir. Carbon isotope ratios are an effective tool to trace the movement and reaction of injected CO_2 in mature oil fields, provided that the injection CO_2 is isotopically distinct. In addition, trends observed in the $\delta^{18}\text{O}$ values of produced water at several wells at Pembina and Weyburn point towards an increasing amount of CO_2 sourced oxygen in the produced waters. Geochemical data taken obtained for fluids from the same wells as this study at Pembina (see companion paper by Shevalier et al.) show further evidence that CO_2 is causing water-rock reactions in the reservoir and provides additional means to detect CO_2 presence in the reservoir.

Further work to quantify the amount of CO_2 sourced oxygen and thus to quantify the amount of CO_2 dissolved in the produced waters using the $\delta^{18}\text{O}$ values is currently being pursued.

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