

Experimental Geochemical Studies Relevant to Carbon Sequestration

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Introduction

Evidence is mounting that rising levels of atmospheric CO₂ will have profound effects on future global climates⁽¹⁻²⁾. Consequently, many experts agree that technologies are needed to slow, and ultimately stop, further buildup⁽³⁻⁵⁾. One of the strategies proposed to achieve this aim is long-term storage (sequestration) of CO₂ in subsurface geologic formations⁽⁶⁻⁷⁾. Currently, the primary candidate sites are active or depleted oil and gas fields, and deep brine formations. Oil and gas reservoirs are promising targets for CO₂ sequestration because: they occur in structural or stratigraphic traps that have been well characterized prior to, and during, oil and gas extraction; they are highly amenable to predictive process modeling using computer codes developed over many decades in the oil and gas industry; and in some fields injection of CO₂ will prolong profitable production of oil or gas⁽⁷⁾. However, deep brine formations could become the predominant geologic hosts for CO₂ sequestration because they are the most common fluid reservoirs in the subsurface and, collectively, they have the largest potential storage capacity of all the candidate geologic sites for CO₂ sequestration⁽⁷⁾.

This paper describes three ongoing CO₂-sequestration research projects in the Chemical and Analytical Sciences Division at the Oak Ridge National Laboratory (ORNL). The wide-ranging activities in these programs are focused on geochemical issues relevant to long-term storage of CO₂ in depleted and active oil and gas fields, and deep brine formations. The main aims of the studies are to determine: (i) the volumetric properties and phase relations of CO₂-CH₄-H₂O fluids, (ii) the kinetics and magnitudes of stable isotope partitioning between calcite and CO₂-enriched formation water, and (iii) the feasibility of using natural and introduced tracers to quantify CO₂ residence time, storage capacity and reaction mechanisms in the subsurface. For

brevity and clarity in the text that follows, the three investigations are discussed separately under the headings:

Project 1: Isotopic and Tracer Studies in Support of the GEO-SEQ Project

Project 2: Isotopic Partitioning in Carbonate-Brine Systems Under Subsurface Conditions

Project 3: Volumetric Properties and Phase Relations of CO₂-CH₄-H₂O Fluids

Objectives and Approach

Project 1. Isotopic and Tracer Studies in Support of the GEO-SEQ Project

ORNL, LBNL and LLNL participate in the NETL-funded GEO-SEQ Project. The overall goal of the ORNL effort is to develop methods that utilize the power of natural and introduced tracers to decipher the fate and transport of CO₂ injected into the subsurface. These techniques are required to calibrate and validate predictive models used for: (1) estimating CO₂ residence time, reservoir storage capacity, and storage mechanisms; (2) testing injection scenarios for process optimization; and (3) assessing the potential for CO₂ leakage from the reservoir.

The basic approach is to utilize a combination of natural and synthetic gas tracers to delineate the subsurface movement of injected CO₂. As it migrates, the CO₂ will induce mass transfer processes through interactions with subsurface materials (e.g., rock, brine, hydrocarbons). These processes can enhance long-term storage of CO₂ and are, thus, important for both predicting and optimizing the effectiveness of geological sequestration of CO₂.

As the injected CO₂ interacts with subsurface geologic materials, its isotopic signature changes, making it a useful natural tracer if: (1) the injection gas stream can be isotopically characterized, (2) the isotopic changes are large enough to be detected during transport, and (3) the changes can be interpreted considering that multiple carbon sinks and sources exist in the subsurface. The first requirement is readily met; however, the second and third are less tractable and require laboratory testing and modeling to determine the feasibility of using CO₂ alone as a tracer.

Project 2. Isotopic Partitioning in Carbonate-Brine Systems Under Subsurface Conditions

Detailed, systematic laboratory experiments are being performed to understand and quantify geochemical reactions that control kinetic and equilibrium isotope partitioning during the precipitation, recrystallization, and replacement of carbonate minerals (calcite, dolomite, siderite) coexisting with CO₂-bearing fluids at conditions encountered in subsurface geologic settings (deep saline formations, sedimentary basins, geothermal systems, etc.). The resulting data can be used to elucidate numerous dynamic geochemical processes involving CO₂ on time scales ranging from hours to thousands of years, ensuing from the injection of large masses of CO₂ into the subsurface. Our specific objectives are to determine the mechanisms and rates of isotope fractionation during (a) precipitation of calcite from a CO₂-bearing solution at low temperatures (25-90°C) and (b) recrystallization and replacement of calcite and dolomite coexisting with CO₂-rich fluid at moderately elevated temperatures (100-300°C). Key experimental variables are: temperature, pressure, P_{CO_2} , ionic strength, and microbial activity. Close monitoring and measurement of solution chemistry, along with detailed mineralogic and crystallographic characterization of the solid phase(s), indicate reaction mechanisms and rates as a function of time. Precise and accurate data on carbon and oxygen isotope fractionation during the precipitation, recrystallization and replacement of carbonate minerals will constrain the

kinetic and equilibrium behavior of the isotopes in subsurface carbonate-forming geochemical reactions. This information is essential for conceptual and numerical modeling of CO₂ sequestration in geologic reservoirs.

Project 3. Volumetric Properties and Phase Relations of CO₂-CH₄-H₂O Fluids

CO₂, CH₄ and H₂O are the predominant volatile constituents of fluids that form and circulate in the Earth's crust. Thus, it is important to understand how these species interact with one another at elevated temperatures and pressures. Experimental and theoretical investigations of the volumetric properties and phase relations of CO₂-CH₄-H₂O mixtures at 50-400°C, 0-100 MPa, indicate limited fluid miscibility—and large, positive excess molar volumes of mixing—over wide ranges of temperature, pressure and fluid composition⁽⁸⁻¹¹⁾. Thus, it is firmly established that CO₂-CH₄-H₂O mixtures are strongly nonideal solutions. However, detailed comparisons of the various data sets and model predictions for CO₂-CH₄-H₂O mixtures also reveal glaring discrepancies that, to date, have not been reconciled. Therefore, new, highly precise and accurate laboratory measurements, and more theoretically rigorous thermodynamic models, are needed to adequately characterize the physicochemical properties of mixed CO₂-CH₄-H₂O fluids.

To measure the volumetric properties of aqueous and carbonic fluids, including binary and ternary CO₂-CH₄-H₂O mixtures, with unprecedented precision and accuracy at temperatures to 500°C and pressures as high as 200 MPa, a unique vibrating U-tube densimeter (VTD) was custom designed and constructed⁽¹²⁾. Fabricated from Inconel 718 tubing, the vibrating tube behaves as a harmonic oscillator, with the period of vibration varying with fluid density. Harmonic oscillation is induced and measured via magnetic coupling between two permanent rod magnets attached to the vibrating tube and four electromagnets fastened to a copper support cylinder. The entire assembly is positioned near the center of a 40" long, DC-powered tube furnace to permit heating to experimental temperature with minimal temperature gradients. High accuracy ($\pm 0.05\%$) positive displacement pumps are used to inject fluids into the vibrating tube.

When the VTD is being used to measure the densities of fluids, readings are taken under isobaric-isothermal conditions, instrument response is calibrated against standard gases (He, Ar, N₂ and H₂O), and short-term instrumental drift is monitored by measuring the density of Ar at the beginning, middle and end of an experimental session⁽⁹⁾. Measurements of pressure and temperature are precise to ± 0.01 MPa and $\pm 0.01^\circ\text{C}$, respectively. Measured densities for pure fluids are believed to be accurate to ± 0.0005 g·cm⁻³. Estimated uncertainties for fluid mixtures range from ± 0.0005 g·cm⁻³ (~1.0%) for low-density fluids to ± 0.0010 g·cm⁻³ (~0.15%) for high-density fluids.

In addition to being a unique, state-of-the-art densimeter, our VTD can also be used to acquire highly precise and accurate liquid-vapor equilibrium (LVE) data for gas-water mixtures at elevated temperatures and pressures^(8,11). This was done for CO₂-H₂O fluids at 300°C using two distinctly different measurement techniques: a "fixed P - T " method⁽⁸⁾, and a "fixed T - X " approach⁽¹¹⁾. In the fixed P - T method, fluid mixtures are pumped through the VTD apparatus at constant temperature, pressure and flow rate. For each mixture, 100-300 measurements of period of vibration (τ) are recorded electronically in a 12-35 minute period. It is consistently observed that the signal from the instrument (τ vs. time, t) is nearly steady for single-phase fluids with compositions far removed from a L - V field. However, as fluid composition approaches a L - V region, τ vs. t becomes increasingly sinusoidal. For two-phase fluids with bulk compositions

0.01-0.02 X (mole fraction gas or water) *inside* a L - V region, τ vs. t is crudely sinusoidal overall, but is interrupted at irregular intervals by large minima or maxima of short duration (generally <35 s). For two-phase fluids with bulk compositions more than $\sim 0.02 X$ inside a L - V field, the instrument signal consists of large, sharp, alternating minima and maxima.

The fixed T - X technique was developed to directly determine the upper baric stabilities of liquid-vapor assemblages in the CO_2 - H_2O system at high subcritical temperatures (~ 275 - 360°C). In this method, the first step is to create an isobaric-isothermal, physically isolated and chemically homogeneous sample of “high-pressure” CO_2 - H_2O fluid of known composition. Fluid pressure (P) is then lowered slowly at constant temperature. Pressure readings and matching values for τ are recorded at 0.1 or 0.2 MPa intervals. When the fluid begins to separate into two phases (liquid + vapor), a distinct inflection is observed in the trend of P vs. τ . Performing such experiments at a fixed temperature in the range 275 - 360°C with fluid compositions at closely spaced intervals produces a complete high- P liquid-vapor boundary curve for the CO_2 - H_2O system at that temperature.

Results

Project 1. Isotopic and Tracer Studies in Support of the GEO-SEQ Project

To use the stable isotope compositions of carbon and oxygen in CO_2 as effective tracers during the injection tests, it is essential to understand how these isotopes partition in response to different process pathways (e.g., mineral reactions, sorption, and aqueous dissolution). We investigated one important isotopic partitioning pathway, that of CO_2 interacting with hydrocarbon-saturated rock (an EOR injection scenario). Hydrocarbon-bearing core was obtained from Chevron’s Lost Hills field (well OB-7). Four samples were selected for study: two were taken in a horizontal orientation (sandy diatomites -H-1450.8 and H-1460.7), the other two in a vertical orientation (diatomites:V-1685.8 and V-1706.0). Approximately 1.5 gms from each core were disaggregated, loaded into a two-zone reaction vessel and reacted with a small quantity ($2.33\text{E-}5$ moles, ~ 0.001 gms) of dry CO_2 (initial $\delta^{13}\text{C}_{\text{PDB}} = 50.4\text{‰}$ and $\delta^{18}\text{O}_{\text{PDB}} = -13.47\text{‰}$). CO_2 was also loaded into a fifth (control) vessel that contained no core material, in order to measure possible partitioning between CO_2 and the vessel walls. These systems were allowed to react for 72 hours at 25°C . A small aliquot of CO_2 was isolated from the solid in the upper portion of each vessel and analyzed isotopically. The CO_2 from the control vessel showed no isotopic variation from the starting composition. Without exception, the CO_2 sampled in the presence of the solid was isotopically enriched in both carbon and oxygen relative to CO_2 lost to the solid (sorption?). CO_2 reacted with sandy diatomites (horizontal orientation) was heavier in $\delta^{13}\text{C}$ by between 3.5 and 4‰ relative to “fixed” CO_2 , whereas enrichments of between 4.0 and nearly 7‰ were observed for CO_2 reacted with diatomite. The $\delta^{18}\text{O}$ enrichments in CO_2 relative to “fixed” CO_2 were similar in magnitude regardless of lithology, ranging from 17 to as high as 35‰. The magnitude of the carbon isotope partitioning is comparable to what others have observed for CO_2 interaction with aqueous solutions. The preliminary conclusion to draw here is that a light isotopic component of CO_2 may be retained in the reservoir leading to progressively heavier isotopic CO_2 farther down the flow path. Clearly, more effort is needed to quantify how these isotopes fractionate as a function of temperature, P_{CO_2} , surface area, hydrocarbon composition, mineral composition, solid-to-volatile mass ratios, and the presence of H_2O ⁽¹³⁻¹⁴⁾.

To supplement the experiments described above, model calculations were conducted to assess the magnitude of carbon isotope change in CO_2 as it reacts with potential reservoir phases. The calculations assumed reaction in a closed system where CO_2 is allowed to interact with varying masses of either a HCO_3^- bearing brine, calcite or hydrocarbon-rich rock (HC; Lost Hills, CA) of unspecified composition. Equilibrium isotope fractionation (fractionation factors taken from Friedman and O'Neil⁽¹⁵⁾) was assumed in all calculations except one set where we used experimental batch-sorption isotope partition data obtained at ORNL on Lost Hills core. Calculations were conducted for 20 and 100°C except for the sorption process, which was based on our 20°C data. The initial carbon isotope value ($\delta^{13}\text{C}_{\text{PDB}}$) of the CO_2 was set at -35‰, typical for CO_2 generated from coal-burning power plants. The initial carbon isotope values for the HCO_3^- fluid and calcite were set at -5 and 0 ‰, respectively, which are typical of values observed in carbonate-hosted brine reservoirs. The HC carbon isotope value (-23‰) is based on what we measured for the Lost Hills core.

The results of these calculations are shown in Fig. 1, where the $\delta^{13}\text{C}_{\text{PDB}}$ values for CO_2 are plotted against the atomic % carbon ratio between CO_2 and the interacting phase of interest (i.e., HCO_3^- , calcite, HC). In a simplistic way, one can think of the extreme left-hand side of the figure as the injection point for the CO_2 , which undergoes reaction with a progressively larger mass of a particular carbon source during transport through the reservoir (left to right across the figure). In all cases the carbon isotope values of CO_2 become less negative through reactions with aqueous HCO_3^- , calcite or HC. The carbon isotope trajectory is determined by (a) temperature, which fixes the fractionation factor between CO_2 and the coexisting phase, and (b) the proportion of carbon in CO_2 relative to that in the interacting phase. All of the cases shown are for binary systems (e.g., CO_2 -calcite, CO_2 - HCO_3^-). However, carbon isotope trajectories for CO_2 interacting with both HCO_3^- and calcite would lie between the respective binary curves for any given temperature scenario. Note that the carbon isotope trajectories for CO_2 interacting with HC-bearing rock vary considerably depending on whether the process is controlled by equilibrium isotope exchange or by sorption; the latter being perhaps more realistic for the relatively low temperatures (30-70°C) at which CO_2 will be injected into EOR or CBM systems.

Through careful selection based on their physical and chemical properties, a combined suite of synthetic tracers can act as a surrogate for injected CO_2 . By their individual and collective transport properties, the tracers provide important information about subsurface mass transfer processes involving CO_2 . Batch reactor and flow-through column tests are planned that utilize a range of reservoir materials and temperature/pressure conditions to (a) evaluate a suite of synthetic tracers and (b) quantify mass transfer coefficients relative to reservoir conditions (e.g., porosity, mineralogy, water saturation, hydrocarbon saturation, temperature, and pressure). Additional tests will be conducted using these same materials and conditions to measure CO_2 isotopic changes. Initially, the natural and applied tracers will be evaluated separately to determine their respective transport characteristics. Later, we will combine them in flow-through column tests and determine correlations between the CO_2 and applied tracers. These experiments will provide a basis for designing and interpreting the results of a pilot field-scale CO_2 injection test. They will also provide key parameters for reservoir modeling and geophysical data interpretation being conducted by others on the project team.

After evaluating the results of published laboratory and field tracer studies, we have selected a suite of gas tracers that appear to have the physical and chemical properties that would make them appropriate for field use in tracking injected CO_2 . The important selection criteria include:

(a) low to zero concentration in the subsurface, (b) detectability at very low concentrations (parts per trillion or less), (c) stable under reservoir conditions, (d) environmentally safe, (e) subject to some of the same mass transfer processes as the injected CO_2 , and (f) amenable to analysis using a single sample and a single analytical method for the entire suite. Based on published studies, we have selected SF_6 and a suite of perfluorocarbons (PFC's) for our initial column studies. Results of these studies will form the basis for final determination of the tracers to be used for the field-scale CO_2 injection test, and evaluations of the results of that test.

Finally, we have completed the basic design for a flow-through column apparatus (Fig. 2) that will allow us to test the relative interactions of the gas tracers with a variety of reservoir materials over ranges of temperature and pressure appropriate for proposed injection scenarios. The column setup relies on the use of a long, thin tube filled with reservoir materials, placed within an oven to provide temperature control. In addition, a backpressure valve is built into the column outlet to allow experiments to be conducted under elevated pressure conditions. The column outflow is shunted to a gas chromatograph equipped with an electron capture device (ECD) by way of two columns, a carbopack column for perfluorocarbon separation and a molecular sieve for SF_6 separation. The PFCs are stripped by the carbopack column, allowing the remaining gas stream to pass through the molecular sieve and be injected into the GC without the clogging effects of the PFCs. The PFCs then elute from the carbopack column and are injected into the GC, allowing all gases to be analyzed from a single sample. The design is similar to that used by Dugstad and others⁽¹⁶⁾ to test gas tracers for reservoir use.

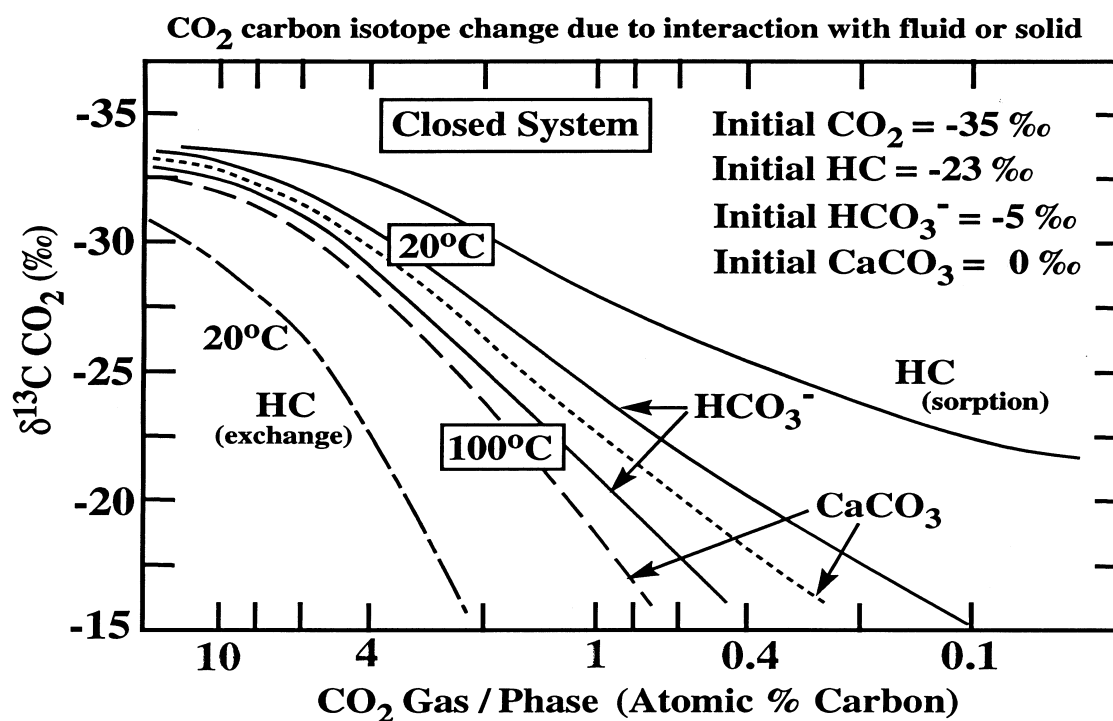


Figure 1. Changes in CO_2 isotopic composition due to fluid/rock interactions. Movements along the x-axis from left to right indicate predicted changes during subsurface transport.

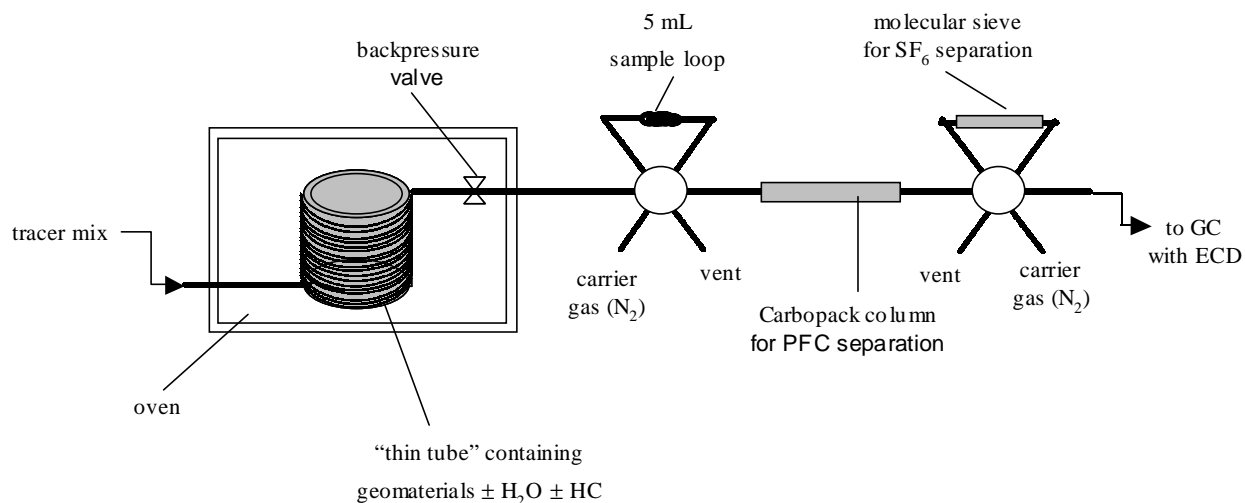


Figure 2. Column apparatus for flow-through gas tracer experiments.

Project 2. Isotopic Partitioning in Carbonate-Brine Systems Under Subsurface Conditions

To understand the isotopic behavior of CO₂ following injection into subsurface geologic formations, the kinetics of oxygen isotope exchange between gaseous CO₂ and various chloride salt solutions (NaCl, KCl, NH₄Cl, CaCl₂, MgCl₂, and AlCl₃) were measured at concentrations to 4 molal and at temperatures from 15 to 50°C. The measured rate constants of isotope exchange, which collectively indicate a first-order reaction, are a factor of 2-20 smaller than corresponding rates for CO₂-H₂O solutions⁽¹⁷⁻¹⁸⁾. It was also observed that isotope exchange rates increased with increasing temperature, with activation energies being ~20 kJ/mol. Our systematic data show that the logarithm of the rate constant determined for the various salt solutions of the same concentration (2 and 4 molal) at 25°C vary linearly with the ionic strength squared divided by the ionic radius (q^2/r), suggesting the possibility of linking the kinetic isotope data to the thermodynamic properties of the salt solutions. These results suggest that oxygen isotope exchange between gaseous CO₂ and saline waters may be a rate-limiting process in subsurface carbonate systems.

We have also investigated carbon and oxygen isotope partitioning during microbial siderite (FeCO₃) precipitation in the temperature range 15-75°C using several strains of anaerobic mesophilic and thermophilic iron-reducing bacteria (Fig. 3). During an early stage of incubation, iron-reducing bacteria rapidly reduced amorphous FeOOH to Fe(II), which in turn was precipitated as siderite, with bicarbonate ion remaining in solution. Subsequently, microbial activity slowed, but the amount of siderite precipitated stayed nearly constant, or decreased slightly. Simultaneously, Fe(II) concentration in the solution decreased, not only due to precipitation of siderite, but also to co-precipitation of large quantities of magnetite.

In the early stages of incubation, the ¹⁸O/¹⁶O isotopic compositions of siderite precipitated from HCO₃-rich (>120mM) solutions were much (>10‰) higher than expected equilibrium

values, but with time $^{18}\text{O}/^{16}\text{O}$ slowly declined toward its equilibrium value. The $^{18}\text{O}/^{16}\text{O}$ isotopic composition of the siderite appears to be controlled by kinetic processes, while its $^{13}\text{C}/^{12}\text{C}$ composition is very close to the equilibrium value. Different strains of bacteria had no effect on isotopic fractionation. After long-term (one month) incubation, it was observed in most cases that $^{18}\text{O}/^{16}\text{O}$ values for biogenically precipitated siderite reached steady-state (equilibrium?) values at 15-75°C. These results are in good agreement with those obtained from experiments on inorganic precipitation of siderite, and from theoretical calculations (Fig.3). However, it was also observed occasionally that, with low bicarbonate concentrations (<60 mM) in the solutions, unreasonably low or high $^{18}\text{O}/^{16}\text{O}$ ratios in siderite persisted even after a one-month incubation period. These results suggest that microbial activities in the subsurface can induce large kinetic isotopic effects in biogenic carbonates, which could be identified long after the carbonates crystallized.

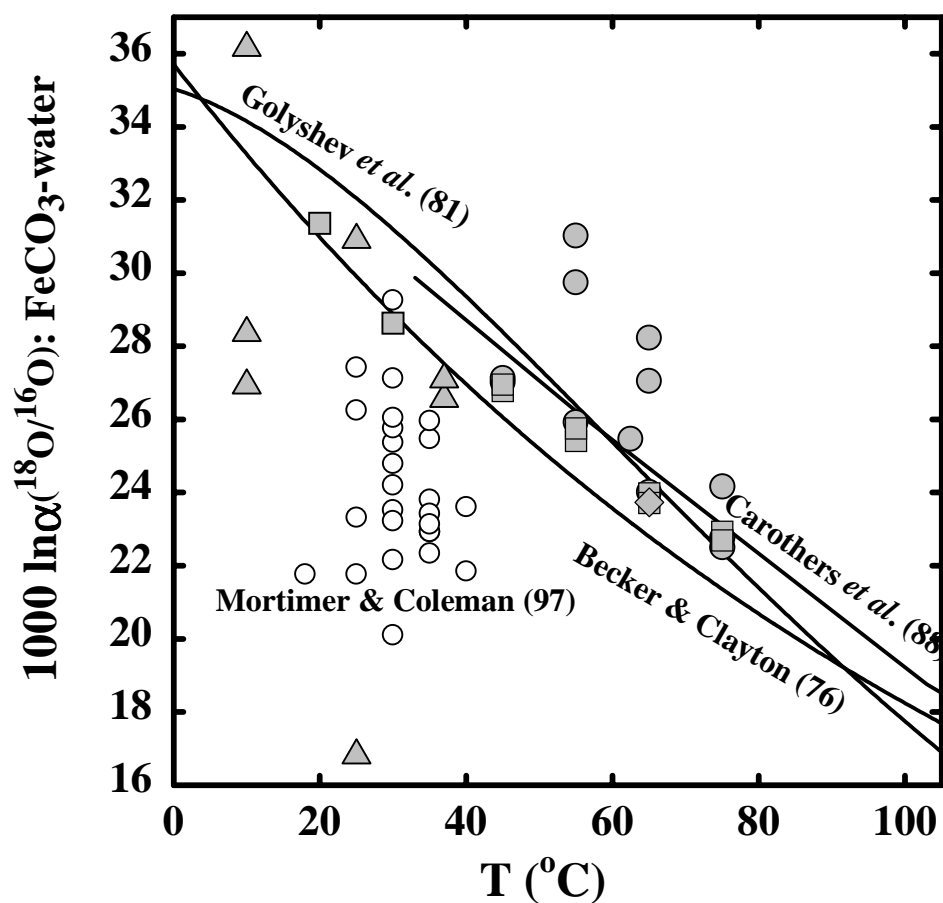


Figure 3. Oxygen isotope fractionation of biogenic siderite precipitated by mesophilic and thermophilic Fe-reducing bacteria⁽¹⁹⁻²²⁾ (after Zhang et al.⁽²³⁾; gray symbols – this study).

Project 3. Volumetric Properties and Phase Relations of CO₂-CH₄-H₂O Fluids

Results obtained from this research are too voluminous to discuss in a short proceedings paper. Therefore, only representative findings are presented here. Data for CO₂-H₂O fluids at 300°C were selected for illustration and discussion because they clearly show that subcritical CO₂-H₂O mixtures are highly nonideal fluids.

Our density and excess molar volume data for CO₂-H₂O fluids at 300°C are plotted in Figs. 4-5. Liquid-vapor coexistence (Figs. 4 and 6) limited the range of composition over which volumetric measurements could be made at pressures from ~8.6 to 56.5 MPa. Nonetheless, the following characteristics of our volumetric data are evident. (1) At 7.44 MPa, fluid density (Fig. 4) increases slowly and continuously from $X_{\text{CO}_2} = 0$ to $X_{\text{CO}_2} = 1$. (2) At pressures from 8.6 to 99.93 MPa, and particularly at pressures below 40 MPa, H₂O-rich fluids are much more dense than CO₂-rich fluids. (3) The densities of CO₂-rich fluids increase sharply from 7.44 to 99.93 MPa. (4) Density vs. X_{CO_2} is nearly linear at 7.44-19.94 MPa, but distinctly nonlinear (concave upward) at higher pressures. (5) At 7.44 MPa, excess molar volume (V^{ex}) vs. X_{CO_2} (Fig. 5a) is nearly symmetric, with a peak value of ~20 cm³/mol at $X_{\text{CO}_2} = 0.5$. (6) With increasing pressure from 7.44 to 9.94 MPa, V^{ex} vs. X_{CO_2} becomes highly asymmetric toward H₂O, with a peak excess molar volume of ~270 cm³/mol at $X_{\text{CO}_2} = 0.1$. This value is ~80% of the molar volume of the mixture, indicating extreme nonideality of the fluid. (7) At pressures above 8.6 MPa (Figs. 5a-b, H₂O-rich fluids have negative excess molar volumes. And finally (8) from 9.94 to 99.93 MPa (Figs. 5b-c): (i) V^{ex} vs. X_{CO_2} for H₂O-rich mixtures becomes progressively less negative; and (ii) excess molar volumes for CO₂-rich fluids are continuously positive, but decrease steadily to values < 5 cm³/mol.

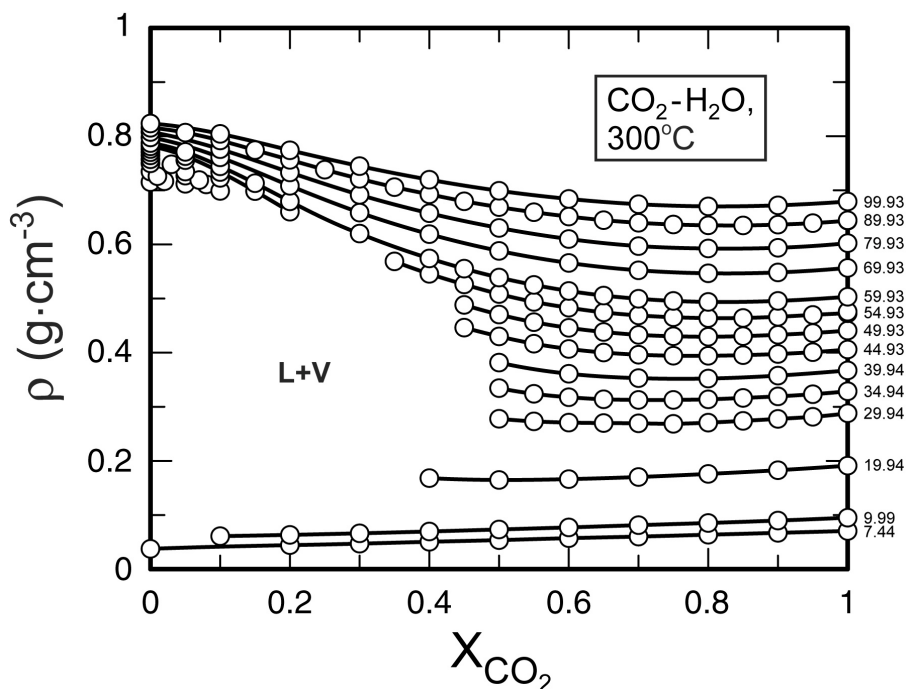


Figure 4. Density (ρ) data for CO₂-H₂O fluids at 300°C, 7.44-99.93 MPa (Seitz et al., in prep). L = liquid, V = vapor.

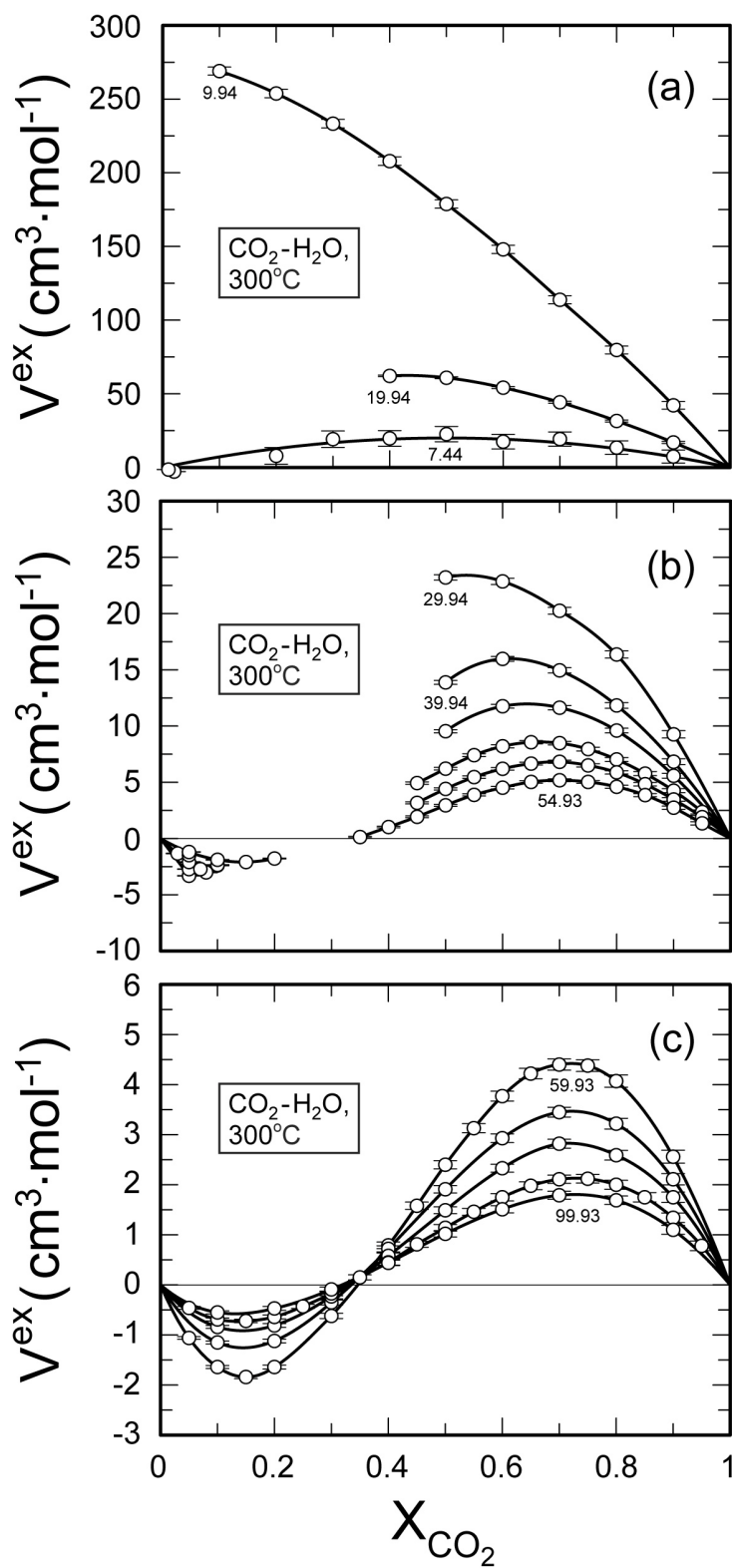


Figure 5. Excess molar volume (V^{ex}) data for CO_2 - H_2O fluids at 300°C , 7.44-99.93 MPa (Seitz et al., in prep.) X_{CO_2} = mole fraction CO_2 .

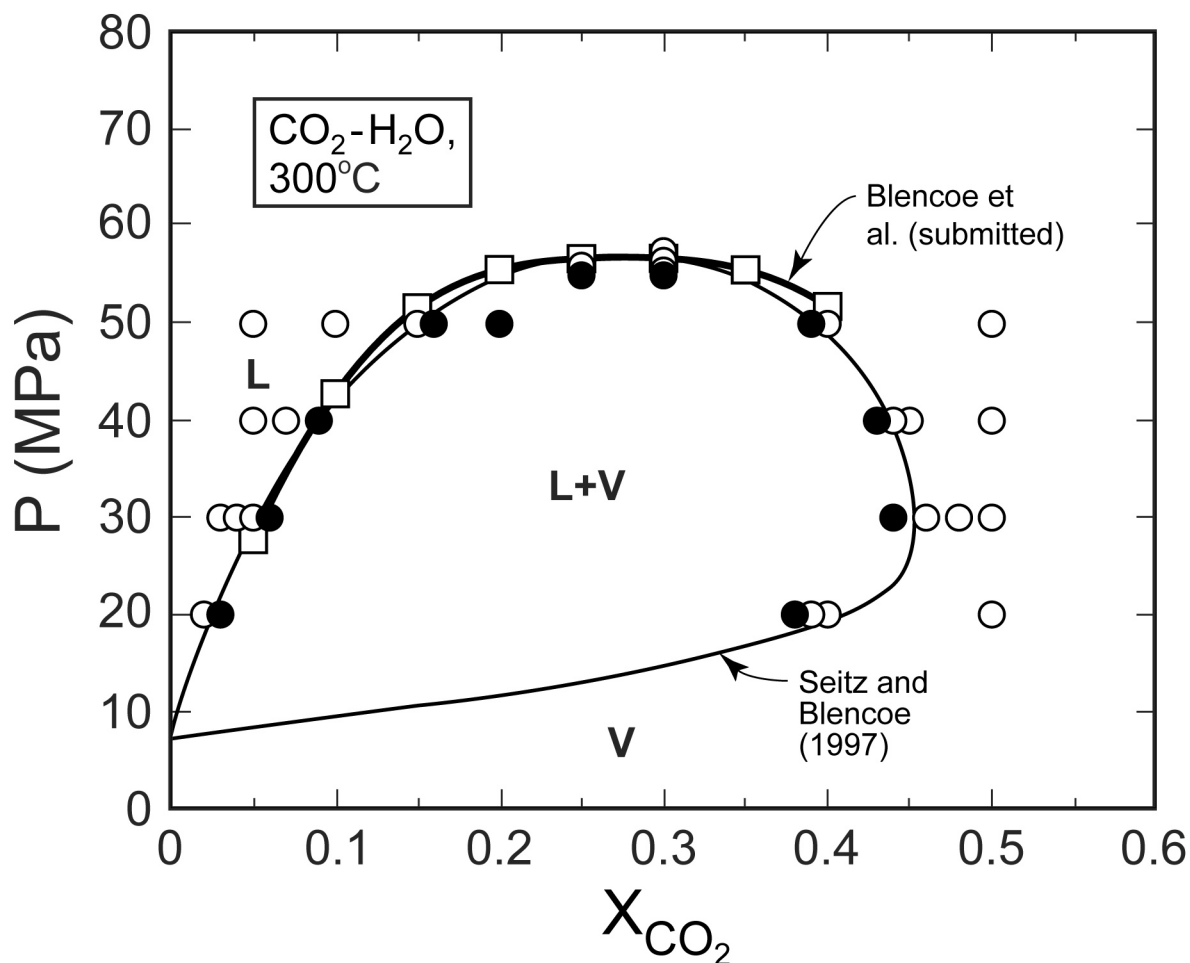


Figure 6. Experimentally determined liquid-vapor (L - V) phase relations for CO_2 - H_2O fluids at 300°C ⁽¹¹⁾.

Our LVE data for CO_2 - H_2O fluids at 300°C (Fig. 6), obtained using the “fixed P - T ” and “fixed T - X ” experimental techniques described above, indicate that the L - V field is balloon-shaped, extending from P_{sat} (the saturation vapor pressure of pure water, ~ 8.6 MPa) to the critical pressure P_c (~ 56.5 MPa), and from $X_{\text{H}_2\text{O}} = 1$ (at P_{sat}) to a maximum X_{CO_2} at approximately $(P_{\text{sat}} + P_c)/2$. The field is bounded by the $L(V)$ (bubble point) and $V(L)$ (dew point) curves. At pressures immediately above P_{sat} the bubble point curve has a steeply positive dP/dX_{CO_2} slope, which decreases steadily with increasing pressure, decreasing to zero as $P \rightarrow P_c$. The P - X_{CO_2} trend of the dew point curve is more complicated. It has a gently positive dP/dX_{CO_2} slope immediately above P_{sat} , which steepens steadily with increasing pressure, becoming infinite near $(P_{\text{sat}} + P_c)/2$ and strongly negative immediately above that pressure. Then, as $P \rightarrow P_c$, it becomes steadily less negative, gradually decreasing to zero.

Future Work

Project 1. Isotopic and Tracer Studies in Support of the GEO-SEQ Project

Future research activities will focus on five main goals:

- (a) construction of flow-through column tracer apparatus and its initial testing using a selected group of rock types and gas tracers.
- (b) evaluation of the gas tracers to determine the relationship between variations in breakthrough behavior and specific transport processes.
- (c) completion of core-gas-fluid isotope exchange experiments, emphasizing both the Lost Hill samples and more generic minerals representative of common reservoir lithologies, such as quartz (sandstone analog), calcite (limestone analog), and montmorillonite (mudstone analog)
- (d) completion of model isotope calculations involving more complex reaction-path scenarios. This activity will also involve an assessment of isotopic studies of gas-bearing reservoir systems that may qualify as analogs for various CO₂ injection scenarios (e.g., brine formations, EOR, CBM, etc.)
- (e) initiation of combined injection of tracers and CO₂ to quantify the relationship between CO₂ partitioning and gas tracer partitioning.

Project 2. Isotopic Partitioning in Carbonate-Brine Systems Under Subsurface Conditions

With our newly constructed “chemo/isot-stat” experimental system, we plan to investigate the kinetics and mechanisms of inorganic carbonate precipitation and associated isotope fractionation from CO₂-rich brines. The chemical and isotopic compositions of brines can be maintained constant during the precipitation of calcite onto seed crystals, so that precipitation rates and isotopic fractionation can be systematically investigated as a function of temperature, salinity, and P_{CO_2} . We plan to conduct our experiments with high salinity (30-100 g/L) brines in the temperature range from 25 to 80°C at high P_{CO_2} (0.5-1 atmosphere), conditions encountered during CO₂ injection into subsurface formation waters. This information is needed for evaluating the fate of injected CO₂, because there is no literature data available under such conditions.

Project 3. Volumetric Properties and Phase Relations of CO₂-CH₄-H₂O Fluids

The experiments and calculations we have performed to determine the thermodynamics and phase relations of supercritical and near-critical CO₂-H₂O fluids have been highly successful, but additional data and modeling are required to permit development of an accurate equation of state (EOS) for these mixtures. Consequently, for the immediate future we plan to: (1) acquire additional volumetric and LVE data for CO₂-H₂O fluids; (2) continue evaluating published EOSs for those mixtures; and (3) develop new polythermal, polybaric models for both supercritical and subcritical CO₂-H₂O mixtures. These objectives will be met by:

- determining the LVE relations of CO₂-H₂O fluids at 275 and 325°C.
- measuring the densities of CO₂-H₂O fluids at 325 and 375°C, 7.5-100 MPa.
- using the P - V - T and LVE data for CO₂-H₂O fluids at 300-400°C acquired in this project, along with compatible experimental data from the literature, to develop a molecular thermodynamic model for CO₂-H₂O fluids at 300-400°C, 0-100 MPa.

Finally, after the thermophysical data base for CO₂-H₂O fluids has been extended sufficiently to permit rigorous EOS development, we will initiate experimentation to measure the densities, excess molar volumes and LVE relations of CH₄-H₂O and ternary CO₂-CH₄-H₂O mixtures at 300-400°C, 7.5-100 MPa.

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