EXPERIMENTAL STUDIES OF OXYGEN ISOTOPE FRACTIONATION IN
THE CARBONIC ACID SYSTEM AT 15°, 25°, AND 40° C

A Thesis

by

WILLIAM CORY BECK

Submitted to the Office of Graduate Studies of
Texas A&M University
in partial fulfillment of the requirements for the degree of

MASTER OF SCIENCE

August 2004

Major Subject: Geology
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Approved as to style and content by:

_________________________    _________________________
Ethan L. Grossman       John W. Morse
(Co-Chair of Committee)         (Co-Chair of Committee)

_________________________     _________________________
Mitchell J. Malone              Richard L. Carlson
(Member)             (Head of Department)

August 2004

Major Subject: Geology
ABSTRACT

Experimental Studies of Oxygen Isotope Fractionation in the Carbonic Acid System at 15°, 25°, and 40°C. (August 2004)

William Cory Beck, B.S., University of Oklahoma

Co-Chairs of Advisory Committee: Dr. Ethan L. Grossman  
Dr. John W. Morse

In light of recent studies that show oxygen isotope fractionation in carbonate minerals to be a function of HCO$_3^-$ and CO$_3^{2-}$ concentrations, the oxygen isotope fractionation and exchange between water and components of the carbonic acid system (HCO$_3^-$, CO$_3^{2-}$, and CO$_2$(aq)) were investigated at 15°, 25°, and 40°C. To investigate oxygen isotope exchange between HCO$_3^-$, CO$_3^{2-}$, and H$_2$O, NaHCO$_3$ solutions were prepared and the pH was adjusted over a range of 2 to 12 by the addition of small amounts of HCl or NaOH. After thermal, chemical, and isotopic equilibrium was attained, BaCl$_2$ was added to the NaHCO$_3$ solutions. This resulted in immediate BaCO$_3$ precipitation; thus, recording the isotopic composition of the dissolved inorganic carbon. Data from experiments at 15°, 25°, and 40°C (1 atm) show that the oxygen isotope fractionation between HCO$_3^-$ and H$_2$O as a function of temperature is governed by the equation:

$$1000 \ln \alpha_{\text{HCO}_3^-\text{H}_2\text{O}} = 2.66 \pm 0.05 \left(10^6T^{-2}\right) + 1.18 \pm 0.52$$
where $\alpha$ is the fractionation factor and $T$ is in kelvins. The temperature dependence of oxygen isotope fractionation between $\text{CO}_3^{2-}$ and $\text{H}_2\text{O}$ is

$$1000 \ln \alpha_{\text{CO}_3^{2-} - \text{H}_2\text{O}} = 2.28 \pm 0.03 \left(10^6 T^{-2}\right) - 1.50 \pm 0.29.$$  

The oxygen isotope fractionation between $\text{CO}_2\text{(aq)}$ and $\text{H}_2\text{O}$ was investigated by acid stripping $\text{CO}_2\text{(aq)}$ from low pH solutions; these data yield the following equation:

$$1000 \ln \alpha_{\text{CO}_2\text{(aq)} - \text{H}_2\text{O}} = 2.52 \pm 0.03 \left(10^6 T^{-2}\right) + 12.12 \pm 0.33.$$  

The kinetics of oxygen isotope exchange were also investigated. The half-times for exchange between $\text{HCO}_3^-$ and $\text{H}_2\text{O}$ were 3.6, 1.4, and 0.25 h at 15°, 25°, and 40°, respectively. The half-times for exchange between $\text{CO}_3^{2-}$ and $\text{H}_2\text{O}$ were 1200, 170, and 41 h at 15°, 25°, and 40°, respectively.

These results show that the $\delta^{18}O$ of the total dissolved inorganic carbon species can vary as much as 17‰ at a constant temperature. This could result in temperature independent variations in the $\delta^{18}O$ of precipitated carbonate minerals, especially in systems that are not chemically buffered.
ACKNOWLEDGMENTS

I thank Dr. Ethan Grossman for all the help and support he has provided throughout the duration of my graduate career. I am especially grateful for his willingness to take on an un-funded project and see it to its completion. I thank Drs. John Morse and Mitch Malone for serving on my committee and for providing many helpful discussions along the way.

I thank Cherie Fischer, Tom Jones, and Keith Gentry for help with isotope analyses and their diligent attention to providing precise, accurate, and timely results. I thank Dwight Gledhill for help with alkalinity and TCO₂ measurements, as well as many helpful discussions. I also thank Kyle Winkler for help in the laboratory, and Erica Bush for help revising early drafts.

Finally, I express my gratitude to my family, who provided emotional and financial support throughout my graduate and undergraduate careers. Without them none of this would have been possible.

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1. INTRODUCTION

Analyses of stable oxygen isotopes have been central in understanding the evolution the Earth’s past climate, oceans, and atmosphere. For instance, Urey (1947), McCrea (1950), Epstein et al. (1953) and many others have shown that temperature and the oxygen isotope composition of the water in which carbonate minerals precipitate control the oxygen isotope composition of the mineral. The temperature dependant fractionation of \(^{18}\)O into carbonate minerals has been used by many investigators to study ancient climate change (e.g., Emiliani, 1955; Popp et al., 1986; Veizer et al., 1986). However, little work has been done to assess if there are other factors that control oxygen isotope fractionation. A recent experimental study of slowly precipitated synthetic carbonate minerals observed that the oxygen isotope composition (\(\delta^{18}\)O) of calcite (CaCO\(_3\)), witherite (BaCO\(_3\)), and octavite (CdCO\(_3\)) can also be a function of the initial HCO\(_3\) and metal ion concentration of the solution (Fig. 1a) (Kim and O’Neil, 1997). Spero et al. (1997) showed that the isotopic composition of foraminiferal calcite can vary as a function of CO\(_3^{2-}\) concentration at a constant temperature (Fig. 1b). There is clearly a need to understand not only the isotopic behavior of mineral-water systems, but also the fractionation between dissolved inorganic carbon species (CO\(_2(aq)\), HCO\(_3^-\), and CO\(_3^{2-}\)) and water.

This thesis follows the style and format of Geochimica et Cosmochimica Acta.
Fig. 1. A. Experimental data from slowly precipitated synthetic calcite showing that the equilibrium fractionation between CaCO₃ and H₂O is dependent upon the initial (equal-molar) concentrations of HCO₃⁻ and Ca²⁺ (modified from Kim and O’Neil, 1997). B. δ¹⁸O of shell carbonate vs. [CO₃²⁻] for the foraminifer Orbulina universa grown at 22°C (modified from Spero et al., 1997).
Chemical interactions among dissolved inorganic carbon species (carbonic acid) are described by the following relationships (Morse and Mackenzie, 1990):

\[
\begin{align*}
\text{CO}_2(g) & \leftrightarrow \text{CO}_2(aq) \quad (1) \\
\text{CO}_2(aq) + \text{H}_2\text{O} & \leftrightarrow \text{H}_2\text{CO}_3 \quad (2) \\
\text{H}_2\text{CO}_3 & \leftrightarrow \text{HCO}_3^- + \text{H}^+ \quad (3) \\
\text{and} \quad \text{HCO}_3^- & \leftrightarrow \text{CO}_3^{2-} + \text{H}^+ \quad (4)
\end{align*}
\]

The relative distribution of these species can be described in terms of pH (Fig. 2). At low pH, \text{CO}_2(aq) is most abundant, and at high pH \text{CO}_3^{2-} is dominate. Each of these species is known to have a different equilibrium oxygen isotope fractionation with water (McCrea, 1950; Usdowski et al., 1991). Thus, pH influences the isotopic distribution in the carbonic acid system.

There have been many studies to understand the carbon isotope fractionation in the carbonic acid system (e.g., Vogel et al., 1970; Mook et al., 1974; Zhang et al., 1995), and oxygen isotope fractionation in the sulfate-water and phosphate-water systems (Hoering and Kennedy, 1957; Lloyd, 1968; O’Neil et al., 2003). In contrast, there are relatively few studies of oxygen isotope fractionation in the carbonic acid system (Halas and Wolacewicz, 1982; Usdowski et al., 1991; Usdowski and Hoefs, 1993), and the latter two studies have been limited to 19º and 25ºC. This paper presents experimentally derived fractionation versus temperature relationships between \text{CO}_2(aq), \text{HCO}_3^-, \text{CO}_3^{2-}, and \text{H}_2\text{O} at 15º, 25º, and 40ºC, as well as kinetics of oxygen isotope exchange.
Fig. 2. Bjerrum diagram showing relative proportions of carbonic acid species as a function of pH at 25°C for total ion activity coefficients equal to unity (modified from Morse and Mackenzie, 1990).
2. MATERIALS AND METHODS

2.1. Overview

Oxygen isotope fractionation was investigated by equilibrating NaHCO₃ solutions at a constant temperature. Small amounts of NaOH or HCl were added to adjust pH. Total alkalinity (Aᵣ), total dissolved inorganic carbon (TCO₂), and pH measurements were made so the carbonic acid speciation could be calculated for each experiment. Once the solutions thermally and isotopically equilibrated, a small amount of the NaHCO₃ solution was mixed with BaCl₂ and NaOH. Quantitative precipitation of BaCO₃ occurred immediately. Because the isotopic composition of rapidly precipitated carbonates records the value of the dissolved carbonate in the system (McCrea 1950), the δ¹⁸O of the BaCO₃ recorded the isotopic value of the dissolved carbonic acid species. Mass balance was used to assess the oxygen isotope fractionation factors for each carbonic acid species.

The BaCO₃ precipitation method worked well for characterizing isotope fractionation between water and CO₃²⁻ and HCO₃⁻, but gave ambiguous results for CO₂(aq)-water fractionation. The isotope fractionation between CO₂(aq) and H₂O was investigated by adding HCl to NaHCO₃ solutions (pH <4.0), such that CO₂(aq) represented greater than 99% of carbonic acid species. Small aliquots of solution were removed and acid stripped; thus, the CO₂(aq) can be directly analyzed as CO₂(g) without an intermediate step. Additionally, BaCO₃ precipitation experiments were run in time series to assess the kinetics of oxygen isotope exchange between carbonic acid species and water.
2.2. Equilibration Experiments with BaCO$_3$ Precipitation

2.2.1. Solution Preparation and Handling

NaHCO$_3$ solutions were prepared to ~0.015 M by adding reagent grade NaHCO$_3$ powder ($\delta^{13}$C$_{PDB} = -20.38 \pm 0.07\%$; $\delta^{18}$O$_{SMOW} = 6.64 \pm 0.09\%$) to distilled deionized (DDI) water that was sparged of CO$_2$(g) by bubbling an inert gas (e.g., N$_2$/Ar). A small amount of 12 N HCl or 1 M NaOH was added to adjust pH. One NaHCO$_3$ solution was prepared to 0.030 M to increase the proportion of NaCO$_3^-$ relative to CO$_3^{2-}$. BaCl$_2$ solutions were prepared to ~0.15 M by adding reagent grade BaCl$_2$·2H$_2$O powder (Fisher lot 027926) to CO$_2$(g) sparged DDI water. Similarly, ~1 M NaOH solutions were prepared by adding reagent grade low-carbonate NaOH pellets to CO$_2$(g) sparged DDI water. All above solutions were mixed in a N$_2$/Ar atmosphere glove bag. These solutions were stored in 25 mL serum bottles with no head space and equilibrated at the experimental temperature (15°, 25°, or 40° ± 0.1°C). Small aliquots of the DDI H$_2$O used to make each NaHCO$_3$ solution were saved for isotopic analyses.

2.2.2. One-Step Equilibration Experiments (Closed System)

All NaHCO$_3$ solutions were thermally equilibrated for a period of one week to many months. After equilibration, a small amount (5-10 mL) of NaHCO$_3$ solution was withdrawn from a stock 25 mL aliquot. The solution was injected into an empty 25 mL Ar-atmosphere serum bottle. An equal molar volume of BaCl$_2$ solution was then added, followed immediately by a small volume (equal to the volume of BaCl$_2$) of NaOH to facilitate the BaCO$_3$ precipitation such that the reaction was essentially instantaneous. Throughout the course of a single experiment, at least four unique BaCO$_3$ precipitations
were conducted on NaHCO₃ stock solutions from at least two different 25 mL stock aliquots. The mass of the BaCO₃ was 95 ± 5% of the expected mass except in a few experiments run at low pH where yields were greater than 70% (see Table 1). In a few experiments, SrCl₂ was also used in the precipitations. The isotopic values of the precipitated carbonates (BaCO₃ and SrCO₃) were essentially identical within precision of the experiment and the differences in acid fractionation factors.

The precipitates were immediately vacuum filtered onto 0.22 µm polycarbonate membranes and rinsed in methanol. The filtration procedure was performed in a N₂/Ar-atmosphere glove bag. The powders were dried overnight in a vacuum desiccator, weighed, removed from the filter membrane with a rubber policeman, and stored in airtight vessels.

The above closed-system procedure was repeated in time series over a period of many months on select high-pH solutions, because of slow exchange rates (see section 3.1.2).

2.2.3. Time-Series Experiments (Open System)

To quantitatively assess the kinetics of oxygen isotope exchange between HCO₃⁻ and H₂O and to explicitly demonstrate isotopic equilibrium, time-series experiments were run. NaHCO₃ solutions were prepared as above (not in a glove bag) in a 1 L RePipet®. Nothing was added to adjust the pH (the solutions were greater than 96% HCO₃⁻; see Table 1). At predetermined time intervals, NaHCO₃, BaCl₂, and NaOH solutions were injected into Ar-atmosphere 25 mL serum bottles. The resulting BaCO₃ precipitate was filtered as above in open atmosphere.
Table 1. Parameters and results for BaCO₃ precipitation experiments.

<table>
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<tr>
<th>Exp.</th>
<th>Temp (°C)</th>
<th>pH (pH)</th>
<th>TCO₂ (mmol/kg)</th>
<th>A₄ (meq/kg)</th>
<th>PCO₂ (mbar)</th>
<th>Ionic Strength (mmol/kg)</th>
<th>X₃CO₃</th>
<th>X₃HCO₃</th>
<th>X₃CO₂H₂O</th>
<th>Yield (%)</th>
<th>δ¹⁸Ο₂SO₂% (SMOW)</th>
<th>δ¹⁸Ο₂BaCO₃% (SMOW)</th>
<th>δ¹⁸Ο₂H₂O% (Std. Dev. (σ))</th>
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(a) Time series experiment
(b) Not used to calculate fractionation factors
Table 1. Continued.

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<th>Aᵢ (meq/kg)</th>
<th>P₀₂ (mbars)</th>
<th>Ionic Strength (mmol/kg)</th>
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<th>X₈ICO₃⁻</th>
<th>X₉CO₂₄₀</th>
<th>Yield (%)</th>
<th>δ¹⁸O₂CO₂ % SMOW</th>
<th>δ¹⁸O₈ICO₃ % SMOW</th>
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</tbody>
</table>

(a) Time series experiment
(b) Not used to calculate fractionation factors
2.3. Calculation of Speciation and Fractionation Factors

The distribution of carbonic acid species in each NaHCO₃ solution was calculated using the EQPITZER program developed by He and Morse (1993). This program was used so the results could be extended to solutions of high ionic strength (i.e. seawater). The PHREEQC version 2.6.0.1 computer program (Parkhurst, 1995) was also used. The calculated species distributions using these two programs are identical within precision of the analyses.

Fractionation factors are reported as “1000 lnα” values where:

\[
\alpha_{A-B} = \frac{\left(\frac{^{18}O}{^{16}O}\right)_A}{\left(\frac{^{18}O}{^{16}O}\right)_B} = \frac{1000 + \delta^{18}O_A}{1000 + \delta^{18}O_B} \]  

(5)

Individual fractionation factors for the carbonic acid species are found by manipulation of the following equations:

\[
1000 \ln \alpha_{\text{BaCO}_3-\text{H}_2\text{O}} = X_{\text{CO}_3^{2-}} 1000 \ln \alpha_{\text{CO}_3^{2-}-\text{H}_2\text{O}} + X_{\text{HCO}_3} 1000 \ln \alpha_{\text{HCO}_3-\text{H}_2\text{O}} + X_{\text{CO}_2(\text{aq})} 1000 \ln \alpha_{\text{BaCO}_3-\text{H}_2\text{O}} \quad \text{(low pH)} \]  

(6)

and

\[
1000 \ln \alpha_{\text{BaCO}_3-\text{H}_2\text{O}} \quad \text{(low pH)} = \frac{2}{3} 1000 \ln \alpha_{\text{CO}_2(\text{aq})-\text{H}_2\text{O}} + \frac{1}{3} 1000 \ln \alpha_{\text{OH}^--\text{H}_2\text{O}} \]  

(7)

where \(X_i\) is the mole fraction of the carbonic acid species. Equation 6 was solved simultaneously for each fractionation factor at each temperature using at least eight unique experiments over a pH range of 2-12 and the multiple regression feature (no intercept model) of the StatView® software package. The \(A_i\) and TCO₂ were used to calculate speciation in all experiments except those at very low pH (< 5), where the \(A_i\)
was below the calibration of the titration. At low pH, TCO2 and pH were used for speciation calculations.

2.4. Analytical Procedures

2.4.1 Isotopic Analyses

Isotopic analyses of the BaCO3 were conducted by reacting the powder with “100%” H3PO4 in a Finnigan Kiel II automated reaction system at 70°C. The resultant CO2 gas was analyzed on a Finnigan MAT 251 isotope ratio mass spectrometer (IRMS). Isotopic results are reported versus SMOW for $\delta^{18}O$. The $\delta^{18}O_{\text{BaCO}_3}$ value was corrected using an “acid fractionation factor” of $1000 \ln \alpha_{\text{CO}_2-\text{CaCO}_3} = 8.12$, and normalized to the laboratory carbonate standard, which had a $\delta^{18}O$ value of -0.14 ± 0.09‰ vs. PDB. No correction was made for the difference in acid fractionation factor between CaCO3 and BaCO3, which is shown to be small (Kim and O’Neil, 1997). Precision for $\delta^{18}O$ of replicate BaCO3 samples taken during each experiment averaged ±0.11‰ (the average of the standard deviations in Table 1).

The isotopic composition of CO2(aq) was found by the “acid-stripping” method, where 1 to 5 mL of the low-pH solution prepared in experiment 11 (see Table 1) was reacted with “100%” H3PO4 in vacuo. The resulting CO2 gas was dried with a dry ice-isopropanol slurry and trapped with liquid nitrogen (see Hassan, 1982). The CO2(g) was analyzed on the MAT 251 mass spectrometer. CO2(g) from the headspace of the serum bottles was also isotopically analyzed.

H2O was analyzed isotopically by equilibration with CO2(g) overnight at 40° or 50°C. The CO2(g) was analyzed on the MAT 251. The $\delta^{18}O$ value of the water was
calculated using the CO$_2$(g)-H$_2$O fractionation equation of O’Neil and Adami (1969). A slight mass correction for the small amount of CO$_2$ used in the equilibration was applied. Samples of VSMOW were analyzed in the same manner. The experiment $\delta^{18}$O$_{H_2O}$ values were normalized to the $\delta^{18}$O of the VSMOW values. Precision for replicate water analyses averaged ±0.09‰.

2.4.2. Other Analyses

Measurements of pH were made using an Orion Model 290A pH meter calibrated to NBS buffers at values of 4, 7, and 10. The pH measurements had an average precision of ±0.07. Total dissolved inorganic carbon (TCO$_2$) measurements were made using a UIC Model 5011 CO$_2$ coulometer (DOE, 1994). Total alkalinity ($A_t$) titrations were made in a open cell water-jacketed vessel with HCl titrant following the method of Gran (1952) using a Metrohm 655 Dosimat and an Orion 720A pH meter (equipped with a Corning semi-micro electrode calibrated to NBS buffers at pH values of 4 and 7) that were interfaced with a computer. Titrations were calibrated against Na$_2$CO$_3$ solutions with known alkalinity. Precision for $A_t$ measurements was better than ±3%, and precision for TCO$_2$ measurements was better than ±7%. Final mineralogy was checked on selected samples using XRD and SEM analyses. No hydrous and/or amorphous BaCO$_3$ phases were detected.
3. RESULTS AND DISCUSSION

3.1. Oxygen Isotope Exchange Kinetics

3.1.1. Oxygen isotope exchange between $\text{HCO}_3^-$ and $\text{H}_2\text{O}$

The kinetics of oxygen isotope exchange between $\text{HCO}_3^-$ and $\text{H}_2\text{O}$ were investigated using the open system time-series method described in section 2.2.3. The experimental parameters are given in Table 1. The $[\text{HCO}_3^-]$ in the solutions used for these experiments was greater than 95% of the TCO$_2$. The “fraction of exchange”, $F$, is calculated using the following equation:

$$F = \frac{\delta^{18}O_t - \delta^{18}O_0}{\delta^{18}O_e - \delta^{18}O_0}$$  \hspace{1cm} (8)

where $\delta^{18}O_t$ is the isotopic value of the BaCO$_3$ at time $t$, $\delta^{18}O_0$ is the initial $\delta^{18}O$ of the NaHCO$_3$, and $\delta^{18}O_e$ is the isotopic value of the BaCO$_3$ after isotopic equilibrium is reached ($\delta^{18}O_e$ is calculated from the “plateau” of the curves in Figure 3). When $F = 0$, no exchange has occurred, and when $F = 1$, exchange is complete. If first order exchange kinetics are assumed, then

$$\ln(1-F) = -k_{avg}t$$  \hspace{1cm} (9)

where $k_{avg}$ is the rate constant (Criss, 1999), which encompasses many forward and backward reactions. Figure 4 shows a plot of $-\ln(1-F)$ versus time. The slopes of the lines are the rate constants at each temperature (Table 2). They are 0.0032, 0.0086, and 0.045 min$^{-1}$ at 15º, 25º, and 40ºC, respectively.
The apparent activation energy \( (E_a) \) can be calculated using the Arrhenius law:

\[
k_{\text{avg}} = A_0 e^{-\frac{E_a}{RT}}
\]  

where \( R \) is the ideal gas constant and \( T \) is the experimental temperature in kelvins.

Figure 5 shows a plot of \( \ln k \) versus \( 1000/RT \). The apparent \( E_a \) is found to be \( 81.6 \pm 3.6 \) kJ/mol.

These results agree well with previous studies. Halas and Wolacewicz (1982) estimate equilibration times to be 8.8 h at 25°C, 2 h at 35°C, and less than 1 h at 45°C. It is precarious to extend these results much beyond the solutions used in this study, because the kinetics of isotope exchange have been shown to be a function of ionic strength (Fortier, 1994; Poulton and Baldwin, 1967). Nevertheless, these experiments had a chemistry that was similar to many natural fresh waters, which could make the results applicable to many natural systems.
Fig. 3. 1000 lnα_{BaCO_3-H_2O} vs. time for oxygen isotope exchange between HCO_3^- and H_2O.

Fig. 4. –ln (1-F) vs. time for HCO_3^-H_2O.
Fig. 5. Arrhenius plot using average rate constants ($k_{avg}$) for $\text{HCO}_3^-$-$\text{H}_2\text{O}$ oxygen isotope exchange ($R^2 = 0.998$).

Table 2. Results for $\text{HCO}_3^-$-$\text{H}_2\text{O}$ exchange kinetics.

<table>
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<th>Exp</th>
<th>Temp. (°C)</th>
<th>$k_{avg}$ ($10^{-3}\text{min}^{-1}$)</th>
<th>$t_{1/2}$ (min)</th>
<th>$t_{\infty}$ (hr)</th>
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<td>15</td>
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</table>
3.1.2. Oxygen isotope exchange between $\mathrm{CO}_3^{2-}$ and $\mathrm{H}_2\mathrm{O}$

“Closed-system” time-series experiments (see section 2.2.2) were run at high pH, such that $\mathrm{CO}_3^{2-}$ represented $>98\%$ of the carbonic acid species (Table 1; Figs. 6 and 7). The average rate constants calculated for $\mathrm{CO}_3^{2-}$-$\mathrm{H}_2\mathrm{O}$ $^{18}\mathrm{O}$ exchange using equation (9) are at least two orders of magnitude less than those for $\mathrm{HCO}_3^-$-$\mathrm{H}_2\mathrm{O}$ exchange (Table 3). The equilibration time for high pH ($>12$) experiments at 15°C is estimated to be 330 d, beyond the range of this study. Consequently, $\delta^{18}\mathrm{O}_e$ at 15°C is calculated from experiments run at lower pH where exchange was more rapid. An Arrhenius plot of the $k_{avg}$ values does not give a satisfactory fit (Fig. 8a). However, if the $k_{avg}$ values are normalized for the $a_{\mathrm{CO}_2(\text{aq})}$ and $a_{\mathrm{OH}^-}$:

$$k' = \frac{k_{avg}}{a_{\mathrm{CO}_2(\text{aq})} a_{\mathrm{OH}^-}} \quad (12)$$

a much better fit is achieved (Fig. 8b). This further substantiates the argument that $\mathrm{CO}_2(\text{aq})$ plays a major role in the oxygen isotope exchange kinetics between $\mathrm{H}_2\mathrm{O}$ and the carbonic acid species (Mills and Urey, 1940).

<table>
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<tr>
<th>Exp.</th>
<th>Temp. (°C)</th>
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<th>$t_{1/2}$ (h)</th>
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Fig. 6. 1000 ln$\alpha_{\text{BaCO}_3\cdot\text{H}_2\text{O}}$ vs. time for high pH experiments where CO$_3^{2-}$ was greater than 97% of the TCO$_2$.

Fig. 7. –ln (1-F) vs. time for exchange between CO$_3^{2-}$ and H$_2$O.
Fig. 8. A. Arrhenius plot for average rate constants of $\text{CO}_3^{2-}$ - H$_2$O exchange. B. Arrhenius plot for rate constants normalized to the activities of CO$_2$(aq) and OH$^-$; better linear fit indicates oxygen isotope exchange between $\text{CO}_3^{2-}$ and H$_2$O is dependent upon CO$_2$(aq).
3.2 Isotopic Fractionation Relations

3.2.1 $\text{HCO}_3^-$-$\text{H}_2\text{O}$ Fractionation

Oxygen isotope fractionation between $\text{HCO}_3^-$ and $\text{H}_2\text{O}$ is calculated from the data in Table 1 and presented in Figure 9 and Table 4. The resulting equation is:

$$1000 \ln \alpha_{\text{HCO}_3^-\text{H}_2\text{O}} = 2.66 \pm 0.05 \left(10^6 T^{-2}\right) + 1.18 \pm 0.52$$  \hspace{1cm} (13).

SrCO$_3$ was precipitated in the same manner as BaCO$_3$ in some experiments run at 25°C and 40°C. The calculated 1000 ln $\alpha_{\text{HCO}_3^-\text{H}_2\text{O}}$ values using SrCO$_3$ are 31.03 ± 0.64 and 28.62 ± 0.07 at 25°C and 40°C, respectively. These values compare well with values calculated using BaCO$_3$ (Table 4) of 31.01 ± 0.18 and 28.29 ± 0.19 at 25°C and 40°C, respectively. Over the temperature range studied, our 1000 ln $\alpha$ values were determined to be about 1‰ greater than those of Halas and Wolacewicz (1982), who used a similar method of precipitating BaCO$_3$ from NaHCO$_3$ solutions (Fig. 9). This discrepancy could be due to a difference in acid-fractionation factors used. Halas and Wolacewicz (1982) used 1000 ln $\alpha_{\text{CO}_2^-\text{BaCO}_3}$ = 10.91, which is 0.72 greater at 25°C than the value for 1000 ln $\alpha_{\text{CO}_2^-\text{CaCO}_3}$ (calcite) of 10.19 at 25°C (Sharma and Clayton, 1965). But as mentioned earlier, studies have shown that the difference in acid-fractionation factors for BaCO$_3$ and CaCO$_3$ is small (about 0.13 at 25°C; Kim and O’Neil, 1997). Because the current results are calculated using the CO$_2$-calcite fractionation, there could be an offset in the results—assuming the offset between the fractionation factors is temperature independent. Furthermore, Halas and Wolacewicz (1982) assumed that their NaHCO$_3$ solutions were 100% HCO$_3^-$. Unfortunately, they did not provide sufficient data to
calculate the speciation of their solutions, but their values are affected to some degree by the small amount of $\text{CO}_3^{2-}$ present.

McCrea (1950) rapidly precipitated calcite from Na$_2$CO$_3$/NaHCO$_3$ solutions; thus, the $\delta^{18}$O of the precipitated calcite records the isotopic composition of the carbonate in the system. $1000 \ln \alpha_{\text{CaCO}_3-\text{H}_2\text{O}}$ values for his data (Table 5) are calculated using the $\delta^{18}$O$_{\text{H}_2\text{O}}$ vs. SMOW (corrected from the reported mean ocean water value) for Lake Michigan water of -5.93‰ (Epstein and Mayeda, 1953) and by assuming his oxygen isotope values are reported against the PDB standard. We used the EQPITZER program to calculate the speciation of McCrea’s solutions using $A_t = [\text{NaHCO}_3] + 2[\text{Na}_2\text{CO}_3]$ and assuming the TCO$_2$ is equal to the initial concentrations of Na$_2$CO$_3$ and NaHCO$_3$. The results compare very well to the present results (Fig. 9; Table 4). However, these data might also be affected by differences in acid-fractionation factors used.

Similarly, the data from the 19°C “type B” experiments of Ustdowski et al. (1991) (Table 5), in which BaCO$_3$ was rapidly precipitated from 0.003M NaHCO$_3$ solutions (the pH was adjusted by addition of HCl or NaOH), were recalculated using the given pH and by assuming the TCO$_2$ is equal to the initial NaHCO$_3$ concentration. The recalculated data agree reasonably well with the present results (Fig. 9; Table 4). The offset could also be due to a difference in acid-fractionation factors. It was not specified what fractionation factor was used.
Table 4. Comparison of results for oxygen isotope fractionation from this study with previous studies.

<table>
<thead>
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<th>Temp °C</th>
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<th>1000 lnα_{CO_{3}^{2–}–H_{2}O}</th>
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<td>5°a</td>
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<td>25.93 ± 0.32</td>
<td>42.43 ± 0.09</td>
</tr>
<tr>
<td>19°b</td>
<td>31.24 ± 0.73 (33.77°f)</td>
<td>25.25 ± 2.49 (18.2)</td>
<td>-56.3</td>
</tr>
<tr>
<td>25°a</td>
<td>31.01 ± 0.18</td>
<td>24.17 ± 0.31</td>
<td>40.49 ± 0.14</td>
</tr>
<tr>
<td>25°c</td>
<td>30.86 ± 0.20</td>
<td>24.58 ± 0.34</td>
<td></td>
</tr>
<tr>
<td>25°d</td>
<td></td>
<td>30.16</td>
<td></td>
</tr>
<tr>
<td>25°e</td>
<td>-34</td>
<td>-18.1</td>
<td></td>
</tr>
<tr>
<td>35°d</td>
<td></td>
<td>28.13</td>
<td></td>
</tr>
<tr>
<td>40°a</td>
<td>28.29 ± 0.19</td>
<td>21.74 ± 0.17</td>
<td>37.80 ± 0.03</td>
</tr>
<tr>
<td>45°d</td>
<td></td>
<td>26.14</td>
<td></td>
</tr>
</tbody>
</table>

(a) This Study
(b) Recalculated from Usdowski et al. (1991); reported values in parentheses
(c) Recalculated from McCrea (1950)
(d) Halas and Wolacewicz (1982); reported values
(e) Usdowski and Hoefs (1993); reported values
(f) After Zeebe (1999)

Table 5. Experimental parameters and isotopic data from previous studies.

<table>
<thead>
<tr>
<th>Exp.</th>
<th>Temp. (°C)</th>
<th>pH</th>
<th>TCO_{2} (mmol/kg)</th>
<th>A_{so} (meq/kg)</th>
<th>P_{CO}_{2} (mbars)</th>
<th>X_{CO_{2}}</th>
<th>X_{HCO_{3}}</th>
<th>X_{CO_{3}^{2–}}</th>
<th>δ^{18}O_{CO_{2}} (SMOW)</th>
<th>δ^{18}O_{HCO_{3}} (SMOW)</th>
<th>1000 lnα_{XCO_{3}–H_{2}O}</th>
</tr>
</thead>
<tbody>
<tr>
<td>B-1°</td>
<td>19</td>
<td>7.67</td>
<td>3.0</td>
<td>2.9</td>
<td>3.4</td>
<td>0.00</td>
<td>0.95</td>
<td>0.05</td>
<td>-8.50</td>
<td>24.0</td>
<td>32.25</td>
</tr>
<tr>
<td>B-2°</td>
<td>19</td>
<td>8.32</td>
<td>3.0</td>
<td>3.0</td>
<td>0.8</td>
<td>0.01</td>
<td>0.98</td>
<td>0.01</td>
<td>-8.50</td>
<td>23.5</td>
<td>31.74</td>
</tr>
<tr>
<td>B-3°</td>
<td>19</td>
<td>9.60</td>
<td>3.0</td>
<td>3.5</td>
<td>0.17</td>
<td>0.83</td>
<td>0.00</td>
<td>-8.50</td>
<td>21.5</td>
<td>29.78</td>
<td></td>
</tr>
<tr>
<td>B-4°</td>
<td>19</td>
<td>10.00</td>
<td>3.0</td>
<td>4.1</td>
<td>0.34</td>
<td>0.66</td>
<td>0.00</td>
<td>-8.50</td>
<td>21.1</td>
<td>29.43</td>
<td></td>
</tr>
<tr>
<td>b</td>
<td>25</td>
<td>7.99</td>
<td>300</td>
<td>300</td>
<td>125</td>
<td>0.01</td>
<td>0.97</td>
<td>0.01</td>
<td>-5.93</td>
<td>24.8</td>
<td>30.47</td>
</tr>
<tr>
<td>b</td>
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<td>8.55</td>
<td>275</td>
<td>287</td>
<td>31.9</td>
<td>0.05</td>
<td>0.95</td>
<td>0.00</td>
<td>-5.93</td>
<td>24.3</td>
<td>29.92</td>
</tr>
<tr>
<td>b</td>
<td>25</td>
<td>8.90</td>
<td>250</td>
<td>275</td>
<td>11.50</td>
<td>0.10</td>
<td>0.90</td>
<td>0.00</td>
<td>-5.93</td>
<td>24.7</td>
<td>30.32</td>
</tr>
<tr>
<td>b</td>
<td>25</td>
<td>10.23</td>
<td>125</td>
<td>213</td>
<td>0.08</td>
<td>0.70</td>
<td>0.30</td>
<td>0.00</td>
<td>-5.93</td>
<td>20.7</td>
<td>26.42</td>
</tr>
<tr>
<td>b</td>
<td>25</td>
<td>11.33</td>
<td>100</td>
<td>200</td>
<td>0.00</td>
<td>0.97</td>
<td>0.03</td>
<td>0.00</td>
<td>-5.93</td>
<td>18.7</td>
<td>24.48</td>
</tr>
</tbody>
</table>

(a) Recalculated from "Type B" BaCO_{3} experiments of Usdowski et al. (1991)
(b) Recalculated from McCrea (1950). Isotope data are for CaCO_{3} (see Table VII in McCrea (1950))
3.2.2. $CO_3^{2-}$ - H$_2$O Fractionation

The isotopic fractionation versus temperature relationship for $CO_3^{2-}$ and H$_2$O is given in Figure 11. The resulting equation is

$$1000 \ln \alpha_{CO_3^{2-}H_2O} = 2.28 \pm 0.03 \left(10^6 T^{-2}\right) - 1.50 \pm 0.29$$  \hspace{1cm} (14)

Ideally, data from experiments in which $CO_3^{2-}$ was >98% of the TCO$_2$ would have been incorporated into the regression to calculate the fractionation factors at each temperature. However, the rate of isotopic exchange between $CO_3^{2-}$ and H$_2$O at 15°C and very high
pH (>12) was too slow to achieve isotopic equilibrium (Fig. 6; see section 3.1.2). A satisfactory fit is achieved using data from 15°C experiments with pH values ranging from 9.5 to 10.5 (20 to 66% CO$_3^{2-}$). The current results agree well with the recalculated results of McCrea (1950) at 25°C and Usdowski et. al (1991) at 19°C (Fig. 10; Table 4). Although the error in the recalculation of the data of Usdowski et al. (1991) is quite large, their reported value of 18.2 for 1000 ln $\alpha_{\text{CO}_3^{2-}-\text{H}_2\text{O}}$ is outside the error of the recalculation. The data of McCrea (1950) might be affected by incomplete isotopic equilibration between CO$_3^{2-}$ and H$_2$O, since his high-pH solutions were allowed to equilibrate a maximum of 7 days before precipitation.

There is concern that the NaHCO$_3$(aq) and NaCO$_3^-$ (aq) ion pairs might have a significant influence on the fractionation factors (O’Neil et. al, 2003). To test this, three 40°C experiments were run with NaHCO$_3$ solutions at high pH (>11) such that [CO$_3^{2-}$] + [NaCO$_3^-$ (aq)] was greater than 93% of the TCO$_2$; the TCO$_2$ and alkalinity were adjusted so that the NaCO$_3^-$ (aq) was ~18, 26, and 45% of the TCO$_2$ (experiments 38B, 40C, and 42, respectively; see Table 1). The resulting 1000 ln $\alpha_{\text{BaCO}_3-\text{H}_2\text{O}}$ value for all three experiments was 22.07. This indicates that weak ion pairs have a negligible effect on the determination of DIC-water fractionation factors.
Fig. 10. 1000 $\ln x_{\text{CO}_3^2-/\text{H}_2\text{O}}$ vs. temperature (kelvins). Data of McCrea (1950) and Usdowski et al. (1991) are recalculated (see text). Error bars are 1 x standard error.

3.2.3. $\text{CO}_2(\text{aq})$-$\text{H}_2\text{O}$ Fractionation

Unlike $\text{CO}_3^2-$ and $\text{HCO}_3^-$, which have a 1:1 oxygen atom ratio relative to $\text{BaCO}_3$, $\text{CO}_2(\text{aq})$ has a 2:3 oxygen ratio relative to $\text{BaCO}_3$. Thus, during precipitation an additional oxygen atom is incorporated into the precipitate $\text{BaCO}_3$. Assuming the precipitation from low-pH solutions occurs via the following reaction:

$$\text{Ba}^{2+} + \text{CO}_2(\text{aq}) + \text{OH}^- \leftrightarrow \text{BaCO}_3 + \text{H}^+. \quad (15)$$
a correction must be made for the contribution of OH$^-$ on the $\delta^{18}$O of BaCO$_3$. At low pH, where CO$_2$(aq) is greater than 99% of the carbonic acid species, the fractionation between CO$_2$(aq) and H$_2$O is given by the manipulation of equation (7) (Usdowski et. al, 1991):

$$1000 \ln \alpha_{\text{CO}_2(aq)-H_2O} = \frac{1}{2} \left( 1000 \ln \alpha_{\text{BaCO}_3^{-1-2H_2O}(\text{lowpH})} \right) - \frac{1}{2} \left( 1000 \ln \alpha_{\text{OH}^--H_2O} \right)$$  \hspace{1cm} (16).

Results using this calculation are shown in Figure 11 for 15 and 25$^\circ$C—temperatures for which data for 1000 $\ln \alpha_{\text{OH}^--H_2O}$ are available (Thornton 1962; Green and Taube, 1963).

Because of the lack of 1000 $\ln \alpha_{\text{OH}^--H_2O}$ data and uncertainty in the reaction mechanism, a different method for calculating the CO$_2$(aq)-H$_2$O fractionation was needed. The “acid-stripping” method (see section 2.4.1) was employed, which allows for the direct measurement of CO$_2$(aq) by conversion to CO$_2$(g) during acid stripping. The results (Fig. 11) yield the equation:

$$1000 \ln \alpha_{\text{CO}_2(aq)-H_2O} = 2.52 \pm 0.03 \left( 10^6 T^{-2} \right) + 12.12 \pm 0.33$$  \hspace{1cm} (17).

The 1000 $\ln \alpha_{\text{CO}_2(aq)-H_2O}$ values agree well with values calculated from Vogel et al. (1970) and are slightly greater than the 1000 $\ln \alpha_{\text{CO}_2(g)-H_2O}$ values of O’Neil and Adami (1969) (Fig. 11). Furthermore, Vogel et al. (1970) show that CO$_2$(aq) is enriched by less than 1‰ in $^{18}$O relative to CO$_2$(g). The CO$_2$(g) in the head space of the serum bottles was also isotopically analyzed. The fractionation of $^{13}$C (1000 $\ln \alpha_{\text{CO}_2(aq)-CO_2(g)}$) between CO$_2$(aq) and CO$_2$(g) is $-1.16 \pm 0.04$, $-1.07 \pm 0.08$, and $-0.90 \pm 0.02$ at 15$^\circ$, 25$^\circ$, and 40$^\circ$C, respectively. This fractionation compares well with Vogel et al. (1970), who obtained values of $-1.12$, $-1.08$, and $-1.01$ at 15$^\circ$, 25$^\circ$, and 40$^\circ$C. The carbon fractionation values
also compare with Zhang et al. (1995), who found $1000 \ln \alpha_{\text{CO}_2(\text{aq})-\text{CO}_2(g)}$ to be -1.21 at $21^\circ\text{C}$.

The current results are in considerable disagreement with the $1000 \ln \alpha_{\text{CO}_2(\text{aq})-\text{H}_2\text{O}}$ value of 56.29 at $19^\circ\text{C}$ reported by Usdowski et al. (1991) (Table 4), who used equation (16) to calculate their value. Given that we obtained similar results using two independent methods, and that these results are supported by the study of Vogel et al. (1970), we believe that our results are correct.

![Graph of $1000 \ln \alpha_{\text{CO}_2(\text{aq})-\text{H}_2\text{O}}$ vs temperature (in kelvins). Data for BaCO$_3$ method are calculated using equation (16).](image)

**Fig. 11.** $1000 \ln \alpha_{\text{CO}_2(\text{aq})-\text{H}_2\text{O}}$ vs temperature (in kelvins). Data for BaCO$_3$ method are calculated using equation (16).
3.3. Discrepancies with Previously Reported Fractionation Factors

Although agreement is shown between results presented in this study and recalculation of the limited data available in the literature, there is considerable disagreement between the reported 1000 ln\(\alpha\) values of this study and those from the pioneering studies of Usdowski et al. (1991) and Usdowski and Hoefs (1993) (Table 4). Figure 12 shows the 1000 ln\(\alpha_{\text{BaCO}_3/c\text{aCO}_3-H_2O}\) values versus pH for data from our study and those of Usdowski and colleagues. The 1000 ln\(\alpha\) values for pH values from 7 to 12 are in relatively good agreement suggesting the discrepancies in fractionation factors are derived from differences in the way the individual fractionation factors are calculated.

Usdowski and colleagues used the relation between 1000 ln\(\alpha_{\text{S-H}_2O}\) and \(\ln \left( \frac{S}{[\text{CO}_2(\text{aq})]} \right)\) (Fig. 13) to calculate their fractionation factors,

\[
\frac{S}{[\text{CO}_2(\text{aq})]} = K_1 + \frac{K_{H_2CO_3}}{[H^+]} + \frac{K_{H_2CO_3}K_{HCO_3^-}}{[H^+]^2} \quad (18),
\]

where \(S = [H_2CO_3] + [HCO_3^-] + [CO_3^{2-}]\) \quad (19).

Equation (18) assumes activity coefficients of unity. The “K’s” refer to the equilibrium constants of the following reactions:

\[
\text{CO}_2(\text{aq}) + \text{H}_2\text{O} \overset{k}{\underset{k'}{\rightleftharpoons}} \text{H}_2\text{CO}_3; \quad K_1 = \frac{k}{k'} \quad (20)
\]

\[
\text{H}_2\text{CO}_3 \leftrightarrow H^+ + \text{HCO}_3^- \quad K_{H_2CO_3} \quad (21)
\]

and

\[
\text{HCO}_3^- \leftrightarrow H^+ + \text{CO}_3^{2-} \quad K_{HCO_3^-} \quad (22).
\]
Fig. 12. 1000 lnα\textsubscript{BaCO}_{3}/CaCO_{3}-H\textsubscript{2}O vs. pH for data from this and previous studies. Data of Usdowski and Hoefs (1993) are calculated from the CaCO\textsubscript{3} data of McCrea (1950).

Fig. 13. 1000 lnα\textsubscript{S-H\textsubscript{2}O} vs. ln (S/[CO\textsubscript{2(aq)}]). Data from this study are 1000 lnα\textsubscript{BaCO}_{3}-H\textsubscript{2}O values from experiments with pH >~8, such that [CO\textsubscript{2(aq)}] < 2%. Similarly, data from Usdowski and Hoefs (1993) are 1000 lnα\textsubscript{CaCO}_{3}-H\textsubscript{2}O values that were calculated from McCrea (1950). Trendline represents equation (23).
The S/[CO₂(aq)] values are calculated at 15°, 25°, and 40°C for our experiments where pH was greater than ~8 (such that 1000 lnαₘ₉=H₂O = 1000 lnα₄BaCO₃-H₂O) using the same sources for equilibrium constants that were used by Usdowski et al., (1991) and Usdowski and Hoefs (1993) (i.e., Harned and Scholes, 1941; Roughton, 1941; Harned and Davis, 1943; Pinsent et al., 1956). Again, there is agreement among the results (Fig. 13). Usdowski et al. (1991) used the linear relationship

\[ 1000 \ln \alpha_{S-H₂O} = -0.610 \cdot \ln \left( \frac{S}{[CO₂(aq)]} \right) + 34.52 \]  

(23)

to calculate the equilibrium fractionations. For instance, Usdowski et al. (1991) show that at pH = pK₆₄H₂CO₃ = 6.39 the mole fraction of HCO₃⁻ is equal to 1, and the value for ln S/[CO₂(aq)] = 0, and 1000 lnαₘ₉=H₂O = 1000 lnα₄HCO₃⁻H₂O = 34.52. Similarly, at pH = pK₆₄H₂CO₃ = 14.20 the system is 100% CO₃²⁻ and ln S/[CO₂(aq)] = 26.769, which yields

1000 lnαₘ₉=H₂O = 1000 lnα₄HCO₃⁻H₂O = 18.19. The 1000 lnα values obtained using equation (23) are much different than those obtained using the mass-balance method we employ (Table 4). Equation (23) implies that fractionation will continue to change even after limiting pH values are reached. The 40°C data from this study with large ln (S/[CO₂(aq)]) (high pH) values seem to reach a limiting fractionation of ~22 (see Fig. 13).

Furthermore, equation (23) does not provide consistent results. At a pH = pK₄HCO₃⁻ = 10.39 the mole fractions of HCO₃⁻ and CO₃²⁻ are equal (X₄HCO₃⁻ = X₄CO₃²⁻ = 0.5) and ln S/[CO₂(aq)] = 9.900, which corresponds to 1000 lnαₘ₉=H₂O = 28.48, but
\[ 1000 \ln \alpha_{\text{H,O}} = 0.5 \times 34.52 + 0.5 \times 18.19 = 26.36 \] (see Table 4 in Usdowski et al., 1991 for data used in the calculations above). Due to these inconsistencies, the method for calculation of fractionation factors used in this study appears to provide better results.

### 3.4. Implications

These new data allow the calculation of the oxygen isotope fractionation between dissolved inorganic carbon and water (and $\delta^{18}O_{\text{DIC}}$) at any pH and temperatures of 15 to 40°C. Figure 14 shows how the $\delta^{18}O_{\text{DIC}}$ could vary in seawater over a pH range of 2-14. It is not suggested that pH has varied by this magnitude over geologic time. However, pH in modern oceans can vary from 7.6 to 8.4 in the water column (Millero, 1996). Over this range, $\delta^{18}O_{\text{DIC}}$ varies by about 1‰ at 25°C. While pH values of surface waters in the modern ocean are relatively constant (8.1 to 8.3) (Millero, 1996), greater variations in ocean-surface pH may have occurred over geologic time. Evidence from boron isotopes suggests that ocean-surface pH could have been as low as 7.4, 21 Myr ago (Spivack et al., 1993) compared with its present value of ~8.2. Zeebe (2001) estimated that ocean surface temperatures for the mid-Cretaceous may have been 2-3.5°C higher than previously thought due to lower pH causing anomalously high $\delta^{18}O$ values in foraminifera. The pH effect on $\delta^{18}O_{\text{DIC}}$ values in unbuffered systems associated with subsurface brines, speleothems, and hot spring deposits may be very important. There is a consistent trend of anomalously low $\delta^{18}O$ values in carbonate concretions that are difficult to explain by diagenetic alteration, high temperature precipitation, or changes in $\delta^{18}O$ value of the water (Mozley and Burns, 1993). These anomalies might be explained by precipitation from high pH fluids. It should be stated that a simple mass balance
calculation using these fractionation factors will not explain the results of Spero et al. (1997) (see Fig. 1B), and the equilibrium fractionations and kinetics could be affected by interactions between dissolved species in seawater (e.g., MgCO$_3$, CaCO$_3$, etc.). Clearly, there is need for more work to investigate the effect of pH on the oxygen isotopic composition of calcite and other carbonate minerals. Nevertheless, this study provides a major step forward in understanding the behavior of oxygen isotopes in carbonate systems.

Fig. 14. Variation of $1000 \ln \alpha_{\text{DIC-H}_2\text{O}}$ (and consequently $\delta^{18}O_{\text{DIC}}$) as a function of pH and temperature. Speciation is calculated using the EQPITZER program with seawater salinity of 35.
4. CONCLUSIONS

BaCO$_3$ precipitation experiments yield reproducible results for oxygen isotope fractionation for HCO$_3^-$-H$_2$O and for CO$_3^{2-}$-H$_2$O. The 1000 $\ln \alpha_{HCO_3^-\text{H}_2\text{O}}$ values obtained in this study are 33.19 ± 0.16, 31.01 ± 0.18, and 28.29 ± 0.19; and 1000 $\ln \alpha_{CO_3^{2-}\text{H}_2\text{O}}$ values are 25.93 ± 0.32, 24.17 ± 0.31, and 21.74 ± 0.17 at 15°, 25°, and 40°C, respectively.

The acid stripping method, where CO$_2$(aq) is directly removed as CO$_2$(g) from low-pH solutions, gave more reliable results than directly precipitating CO$_2$(aq) as BaCO$_3$. The 1000 $\ln \alpha_{CO_2(aq),H_2O}$ values are 42.43 ± 0.09, 40.49 ± 0.14, and 37.80 ± 0.03 for 15°, 25°, and 40°C, respectively.

Rate constants for oxygen isotope exchange between HCO$_3^-$-H$_2$O in ~15 mM NaHCO$_3$ solutions were 3.2, 8.6, and 45 (10$^{-3}$ min$^{-1}$) at 15°, 25°, and 40°C, respectively. Isotope exchange between CO$_3^{2-}$ and H$_2$O is 100 to 300 times slower than isotope exchange between HCO$_3^-$ and H$_2$O. The average rate constants for isotope exchange between CO$_3^{2-}$ and H$_2$O were more consistent if normalized to the activities of CO$_2$(aq) and OH$^-$ in the system. Experiments to investigate relative rates of exchange between carbonic acid species and water showed exchange was much faster at low pH (high P$_{CO_2}$) than at high pH (low P$_{CO_2}$). This confirms that the kinetics of oxygen isotope exchange are largely determined by the activity of CO$_2$(aq) in the system.
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VITA

William Cory Beck

Permanent Address:
   526 North Oak Street
   Hennessey, Oklahoma 73742

Education:
   M.S. Geology, 2004, Texas A&M University, College Station, Texas
   B.S. Geology, 2001, University of Oklahoma, Norman, Oklahoma

Professional Experience:
   Dominion Exploration and Production, Oklahoma City, Oklahoma: Associate
   geologist. June 2004 to present.

   Texas A&M University, Department of Geology and Geophysics: Taught physical
   geology and petroleum geology labs. August 2001 to December 2003.

   Southwestern Energy Company, Houston, Texas: Summer intern,
   exploration/development in Delaware Basin, New Mexico. May 2003 to August
   2003.

   BP, Houston, Texas: Summer intern, development Gulf of Mexico Shelf. May 2002
   to August 2002.

   Mewbourne Oil Company, Amarillo, Texas: Summer intern, development Anadarko

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