Hydrogen and Oxygen Isotope Fractionation Between Brucite and Aqueous NaCl Solutions from 250 to 450°C

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W. C. Shanks III

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Hydrogen and oxygen isotope fractionation between brucite and aqueous NaCl solutions from 250 to 450°C

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Abstract—Hydrogen and oxygen isotope fractionation factors between brucite and aqueous NaCl solutions (1000lnαbr-sw) have been calibrated by experiment from 250 to 450°C at 0.5 Kb. For D/H fractionation, 1000lnαbr-sw values are as follows: −32 ± 6‰ (250°C, 3.2 wt% NaCl), −21 ± 2‰ (350°C, 10.0 wt% NaCl), and −22 ± 2‰ (450°C, 3.2 wt% NaCl), indicating that brucite is depleted in D relative to coexisting aqueous NaCl solutions. These results are in good agreement with previous D/H fractionation factors determined in the brucite-water system, indicating that any effects of dissolved salt on D/H fractionation are relatively small, particularly in solutions near seawater salinity. The maximum salt effect (+4‰) was observed in 10.0 wt% NaCl solutions at 350°C, suggesting that the addition of dissolved NaCl increases the amount of deuterium fractionated into mineral structures. For 18O/16O fractionation, 1000lnαbr-sw values in 3.0 wt% NaCl solutions are −6.0 ± 1.3‰, −5.6 ± 0.7‰ and −4.1 ± 0.2‰, at 250, 350, and 450°C, respectively, and −5.8 ± 0.6‰ in 10.0 wt % NaCl at 350°C. These data indicate that brucite is depleted in 18O relative to coexisting aqueous NaCl solutions and that the degree of depletion decreases slightly with increasing temperature and is not strongly dependent on salinity. We calculated 18O/16O brucite-water fractionation factors from available calibrations of the salt-effect on 18O/16O fractionation between coexisting phases. The resulting values were fit to the following equation that is valid from 250 to 450°C

\[
1000 \ln \alpha_{\text{br-sw}} = 9.54 \times 10^6 T^{-2} - 3.53 \times 10^4 T^{-1} + 26.58
\]

where \(T\) is temperature in Kelvin. These new data have been used to improve the prediction of 18O/16O fractionation factors in the talc-water and serpentine-water systems by modifying existing empirical bond-water models. The results of this analysis indicate that the 818O composition of talc-brucite and serpentine-brucite pairs could be used as a geothermometer and that these coexisting phases should display the following order of 18O enrichment: talc > serpentine > brucite.

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1. INTRODUCTION

The stable isotope composition of minerals and fluids has been widely used to study rock alteration processes in hydrothermal environments. Primary goals of such studies include constraining the origin of minerals and fluids and defining temperature during fluid-rock interaction (Taylor, 1974). This requires that equilibrium isotope fractionation factors between minerals and fluids be known as a function of temperature and fluid composition. Because most geologic fluids are not pure water, the calibration of mineral-fluid fractionation factors in temperature and fluid composition is particularly important.

Although D/H and 18O/16O fractionation factors have been determined by experiment for a large number of mineral-water pairs (O’Neil, 1986), data for minerals in the MgO-SiO2-H2O system are lacking. A notable example is brucite. Fractionation of 18O and 16O between brucite and water has not been calibrated by experiment despite the fact that brucite is associated with low to moderate grade metamorphism of ultramafic and carbonate rocks and has a well defined composition and structure. The D/H fractionation factor between brucite and pure water has been calibrated by experiment from 100°C to 510°C (Satake and Matsuo, 1984), but no data exists for D/H fractionation in systems containing brucite and salt solutions. Moreover, empirical bond-type models have been used to calculate 18O/16O mineral-water fractionation factors for other hydrous phases in the MgO-SiO2-H2O system, such as talc and serpentine, which have been difficult to calibrate by experiment (Savin and Lee, 1988). Results of these calculations are dependent on the quality of bond-water fractionation factors. One of the most poorly known factors is that involving the bonding of Mg with the hydroxyl anion as in the brucite structure (Savin and Lee, 1988). Thus, predictions of 18O/16O fractionation factors based on the empirical bond-water approach would be greatly improved by experimental calibration of 18O/16O fractionation in the relatively simple brucite-fluid system.

Recent experiments by Horita et al. (1993a,b, 1995) have defined the effect of dissolved salt on D/H and 18O/16O fractionation between liquids and vapors to 350°C. Extension of their results to mineral-fluid systems suggests that D/H fractionation factors for all mineral-fluid pairs should become more positive with increasing dissolved salt concentration. For 18O/16O fractionation, the opposite effect has been measured, and this has been further supported by experiments in the calcite-water ± NaCl system at 300°C and 1 kbar (Horita et al., 1995). Other mineral-fluid equilibration studies have yielded different results, particularly with regards to the magnitude of the salt effect on D/H fractionation (Graham and Sheppard, 1980). It has been suggested that these discrepancies are related to...
250 to 450°C at 0.5 kbar. The results provide the first experi-
ments (Horita et al., 1995). As a consequence, more studies of
such as epidote in some mineral-fluid isotope exchange experi-
ments. Consequently, values of α that vary as a function of
time reflect uncertainties associated with experimental and analytical
techniques in addition to assumptions inherent in the partial exchange
approach.

2. EXPERIMENTAL

2.1. Approach

The fractionation factor between mineral and fluid (α_{mineral-fluid}) can be

\[
\alpha_{\text{mineral-fluid}} = \frac{\delta_{\text{mineral}} - 1000}{\delta_{\text{fluid}} - 1000} \tag{1}
\]

where δ_{mineral} and δ_{fluid} refer to the isotopic composition of coexisting
mineral and fluid samples, respectively, in standard δ notation as follows:

\[
\delta_{\text{sample}} = \frac{R_{\text{sample}} - R_{\text{standard}}}{R_{\text{standard}}} \times 1000 \tag{2}
\]

In Eqn. 2, R_{sample} and R_{standard} refer to the D/H or 18O/16O ratio of the
sample and standard, respectively. All δ values are reported in units of
per mil (‰) relative to the SMOW standard.

The partial exchange technique (Northrop and Clayton, 1966; Su-
zuoki and Epstein, 1976) was used in this study to retrieve equilibrium
fractionation factors. This technique involves the use of companion runs, defined here as two experimental charges that are identical in
every respect except for the isotopic composition of the initial fluids. In this investigation, the initial fluids were prepared to be either isotopi-
cally simple minerals such as brucite.

Table 1. Hydrogen isotope data for brucite-water + NaCl Exchange experiments.*

<table>
<thead>
<tr>
<th>Days</th>
<th>T (°C)</th>
<th>NaCl wt. %</th>
<th>Wt. br grams</th>
<th>Wt. sw grams</th>
<th>δDbr</th>
<th>δDsw</th>
<th>Wt. br grams</th>
<th>Wt. sw grams</th>
<th>δDbr</th>
<th>δDsw</th>
<th>10⁶lnα_{br-sw} % ex</th>
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<tr>
<td>0a</td>
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<td>3.0</td>
<td>0.007</td>
<td>1.5316</td>
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<td>−18</td>
<td>0.2009</td>
<td>1.5178</td>
<td>−74</td>
<td>−125</td>
<td>(−36 ± 79.7)</td>
</tr>
<tr>
<td>27</td>
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<td>3.0</td>
<td>0.006</td>
<td>1.5264</td>
<td>−53</td>
<td>−19</td>
<td>0.2006</td>
<td>1.4766</td>
<td>−129</td>
<td>−123</td>
<td>−28</td>
</tr>
<tr>
<td>210</td>
<td>350</td>
<td>10.0</td>
<td>0.2012</td>
<td>1.5801</td>
<td>−61</td>
<td>−25</td>
<td>0.2043</td>
<td>1.5948</td>
<td>−135</td>
<td>−126</td>
<td>−23</td>
</tr>
<tr>
<td>32</td>
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<td>0.2061</td>
<td>1.5809</td>
<td>−49</td>
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<td>0.2003</td>
<td>1.5822</td>
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<td>−126</td>
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<tr>
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<td>10.0</td>
<td>1.25</td>
<td>0.2056</td>
<td>1.2627</td>
<td>−22</td>
<td>−20</td>
<td>0.2022</td>
<td>1.5838</td>
<td>−142</td>
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</tr>
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<td>3.0</td>
<td>0.2045</td>
<td>1.2658</td>
<td>−42</td>
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<td>1.2655</td>
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<td>−20</td>
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<td>1.2591</td>
<td>−141</td>
<td>−122</td>
<td>−20</td>
</tr>
</tbody>
</table>

* The subscripts ‘br’, ‘sw’, and ‘w’ refer to brucite, salt-water, and pure water, respectively. Accordingly, the subscripts ‘br-sw’ indicate 1000lnα values in the brucite-water + NaCl and brucite-water systems, respectively. The values in parenthesis represent mean 1000lnα values for each condition.

The initial isotopic composition of brucite and NaCl solutions is indicated by the data at 0 days of reaction.

* The initial isotopic composition of brucite and NaCl solutions has been investigated by experiment from

<table>
<thead>
<tr>
<th>Days</th>
<th>T (°C)</th>
<th>NaCl wt. %</th>
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<th>δDsw</th>
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<td>30</td>
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<td>1.2591</td>
<td>−141</td>
<td>−122</td>
<td>−20</td>
</tr>
</tbody>
</table>

The experiments were performed using flexible gold capsules (1 cm
outside diameter, 0.13 mm wall thickness, 5 cm length, 4 mL internal
volume) pressurized within steel pressure vessels. The gold capsules
were welded at one end before loading with 0.20 g brucite and 1.25 g
Fine-grained reagent grade Mg(OH)₂ was used in all experiments. X-ray
diffraction (XRD) analyses indicate that this material is crystal-
line. Previous isotopic exchange experiments in the brucite-water sys-
tem have revealed no systematic difference in the D/H fractionation
factor obtained by using synthetic and natural brucite samples (Satake
and Matsuo, 1984). Fluids with salinities of 3.0 wt% NaCl and 10.0
wt% NaCl were prepared from Milli-Q water, reagent grade NaCl,
and water isotopically enriched or depleted in D and 18O. The isotopic
compositions of all reactants are given in Tables 1 and 2.
fluid (450°C experiments) or 1.50 g fluid (250 and 350°C experiments). A relatively high fluid/brucite mass ratio (6.25–7.50) was adopted to minimize changes in the isotopic composition of the fluid during an experiment, thereby reducing the potential for isotopic zonation within the brucite. After loading the solid and fluid reactants, the open end of the gold capsule was sealed by a metal seal which was then welded while submerging the previously welded end in liquid nitrogen to prevent evaporation of the fluid. For each experiment, three or four gold capsules with identical solid and fluid reactants were prepared. These capsules were weighed and loaded into separate pressure vessels along with the companion capsules for each temperature + brucite + salinity condition.

The internal pressure of each gold capsule was externally adjusted by pumping water into the pressure vessel. Pressure was maintained at 0.5 kbar for all experiments. Temperature was monitored by a thermocouple placed in a well that extended into the pressure fluid surrounding the gold capsules. In addition, other thermocouples were attached to the outside of each pressure vessel along its entire length to ensure that there were no thermal gradients during the experiments. All pressure vessels were then placed into a single tube furnace. Using this design, the temperature inside the pressure vessels was controlled to ±2°C.

The isotopic compositions of brucite and fluid were determined as a function of time by removing a single pressure vessel from the furnace at selected times, without disturbing the temperature and pressure condition of the remaining vessels. Reaction times varied from 14 to 225 days. The pressure vessel was cooled to room temperature in less than 10 min by exposure to a cold gas stream followed by immersion in a water bath. Because the solubility of brucite increases with decreasing temperature and is extremely small in the near neutral pH fluids used for this study (Walther, 1986), brucite precipitation during quench can not occur while any brucite dissolution would be relatively minor with little effect on the isotopic composition of the fluid and solid phases.

Immediately after cooling, each capsule was weighed and then punctured with a hypodermic needle to transfer the fluid to a glass gas-tight syringe. Each fluid sample was then passed through a 0.22 μm syringe filter to remove any particulates and sealed in a glass ampule for chemical analyses. The solids were dried at 40°C and then stored for isotopic, XRD, and SEM analyses. Dissolved Cl concentration was determined for all fluid samples using ion chromatography. A large decrease in the Cl concentration indicated that a capsule had leaked during an experiment, and all results from such a capsule were discarded. All isotopic analyses were performed at the USGS in Denver using a Finnigan Mat 252 mass spectrometer. All brucite samples were dried overnight in a vacuum at 80°C. Water was then liberated from brucite for D/H measurements by heating each sample in a Pt boat using an induction coil followed by a conversion to H2 gas through reaction with U (Godfrey, 1962). The 18O/16O composition of brucite was determined by the BrF5 technique (Clayton and Mayeda, 1963). For initial fluid reactants, the D/H composition was determined by zinc reduction following the techniques of Coleman et al. (1982), and the 18O/16O composition was determined using the CO2 equilibration approach of O’Neil et al. (1975). Analytical precision for isotope analyses were approximately ±0.1‰ and ±1.0‰ for 18O/16O and D/H, respectively. Because the experiments were conducted in a closed-system at high fluid/brucite mass ratios, changes in the isotopic composition of the fluids were small compared to those for brucite. As a consequence, the isotopic composition of the fluid after reaction was calculated by material balance using the isotopic composition of the brucite measured after reaction.

### Table 2. Oxygen isotope data for brucite-water + NaCl exchange experiments.*

<table>
<thead>
<tr>
<th>Days</th>
<th>T (°C)</th>
<th>NaCl wt. %</th>
<th>Wt. br grams</th>
<th>Wt. sw grams</th>
<th>δ18Osw</th>
<th>δ18Obr</th>
<th>δ18Obr</th>
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<td>-3.4</td>
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<td>-5.8</td>
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</tr>
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</table>

* The subscripts ‘‘br’’, ‘‘sw’’, and ‘‘w’’ refer to brucite, salt-water, and pure water, respectively. Accordingly, the subscripts ‘‘br-sw’’ and ‘‘br-w’’ indicate 1000lnδ values in the brucite-water + NaCl and brucite-water systems, respectively. The values in parenthesis represent mean 1000lnδ values for each condition.

* The initial isotopic composition of brucite and NaCl solutions is indicated by the data at 0 days of reaction.
erned primarily by dissolution-recrystallization, rather than volume diffusion. Moreover, at each temperature the extent of D/H exchange between brucite and the NaCl fluid was similar to the extent of $^{18}$O/$^{16}$O exchange (Figs. 2 and 3). These data are consistent with a dissolution-recrystallization mechanism since hydrogen diffusion is generally thought to be more rapid than oxygen diffusion in mineral-fluid systems (Cole and Ohmoto, 1986). A two-stage process involving volume diffusion after an initial rapid recrystallization process (Matthews et al., 1983) cannot be ruled out although it is likely that volume diffusion would be quite slow at the temperatures of these experiments.

Values of $\alpha_e$ were computed as a function of time for each experiment. Because the extent of isotope exchange increased only slightly after the first sampling occasion in most experiments, we adopted the mean $\alpha_e$ value as the most accurate fractionation factor at each condition. This approach allowed us to better assess the uncertainties associated with the partial exchange technique.

3.1. Hydrogen Isotopes

Hydrogen isotope data in the brucite-water + NaCl system are summarized in Table 1. The extent of D/H exchange was dependent on temperature, varying from 76% after 210 days of reaction at 250°C, to 100% after only 14 days of reaction at 450°C (Fig. 2). Values of $10^3 \ln \alpha_{br-sw}$ calculated as a function of time are characterized by less variation at higher temperature (Table 1), a result that can be attributed to the fact that uncertainties are magnified when applying the partial exchange technique at relatively low extents of isotopic exchange (Northrop and Clayton, 1966). Accordingly, standard deviations for mean values of $10^3 \ln \alpha_{br-sw}$ vary from $\pm 6^\circ_e$ at 250°C to $\pm 2^\circ_e$ at 450°C. Examination of Fig. 4 shows that $10^3 \ln \alpha_{br-sw}$ values are less than zero at 250° to 450°C, indicating that brucite is depleted in D relative to coexisting NaCl solutions. Decreases in $10^3 \ln \alpha_{br-sw}$ values from 450 to 250°C in 3.0 wt% NaCl solutions also indicate that the degree of depletion increases with decreasing temperature.

In isotopic systems containing solids and aqueous solutions, the effect of dissolved salt (I) on mineral-water fractionation factors for any pair of stable isotopes can be written as

$$10^3 \ln \Gamma = 10^3 \ln \alpha_{m-sw} - 10^3 \ln \alpha_{m-w}$$

where $10^3 \ln \alpha_{m-sw}$ and $10^3 \ln \alpha_{m-w}$ refer to fractionation factors in the mineral-water + salt and mineral-water systems, respectively. Thus, a direct comparison of the fractionation factors obtained here in NaCl solutions with those obtained by Satake and Matsuo (1984) in pure water serves to define the effect of dissolved salt on D/H fractionation. Such a comparison (Fig. 4) shows that the fractionation factors reported in this study are in

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Fig. 1. (a) SEM image of initial reagent grade brucite used for isotope exchange experiments. The material is extremely fine-grained, and individual crystals are not discernible at this magnification. (b) SEM image of brucite after 210 days of reaction in 3.0 wt% NaCl solution at 250°C. Large euhedral brucite crystals have grown at the expense of the initial fine grained material. This analysis suggests that isotope exchange occurred by a dissolution-recrystallization mechanism as opposed to volume diffusion.
reasonable agreement with those measured by Satake and Matsuo (1984) in the brucite-water system, which suggests that the effect of dissolved salt on D/H fractionation between minerals and hydrothermal solutions with near seawater salinity is small (within the error of the measured fractionation factors). The most statistically significant discrepancy occurs at 350°C in the 10.0 wt% NaCl solution, where our value of $10^3 \ln a_{\text{br-sw}}$ appears to be more positive than the corresponding value of $10^3 \ln a_{\text{br-w}}$ measured by Satake and Matsuo (1984). At this condition, uncertainties associated with the fractionation factors are sufficiently low and the salinity sufficiently high, to more clearly resolve how the addition of salt changes D/H fractionation between minerals and NaCl solutions (see Fig. 4). Application of Eqn. 5 yields a $10^3 \ln G(D)$ value of $+14\‰$ at this condition, suggesting that the addition of dissolved NaCl to mineral-water systems increases the amount of D fractionated into the mineral structure.

Horita et al. (1995) measured the salt-effect on D/H fractionation factors between coexisting phases by equilibrating liquids and vapors in the water $+\mathrm{NaCl}$ system and derived the following empirical relationship:

$$10^3 \ln \Gamma(D) = m(0.01680T - 13.79) + 3255/T$$

where $m$ is the molality of dissolved NaCl, and $T$ is temperature (K). At 350°C for a 10.0 wt% NaCl solution, Eqn. 6 yields a $10^3 \ln \Gamma(D)$ value of $+3.3\‰$, in good agreement with our value ($+4.0\‰$) obtained from Eqn. 5. At 250°C for a 3.0 wt% NaCl solution, Eqn. 6 yields a $10^3 \ln \Gamma(D)$ value of $+0.7\‰$, which is well within the uncertainty of our measurements. It is important to note that Eqn. 6 has been calibrated by Horita et al. (1995) to a maximum temperature of 350°C using the liquid-vapor equilibration approach. As a consequence, the effect of dissolved salt on D/H fractionation is still not well constrained at higher temperatures in the supercritical region for hydrothermal fluids. Although we cannot statistically constrain a precise value for $\Gamma$ at 450°C, we can use the uncertainties in fractionation factors reported here and by Satake and Matsuo (1984) to place limits on the range of possible $\Gamma$ values at this condition. This analysis constrains $10^3 \ln \Gamma(D)$ to be less than $+4\‰$, suggesting that any effect of dissolved salt on D/H fractionation is small for hydrothermal fluids with near seawater salinity at temperatures up to 450°C.

### 3.2. Oxygen Isotopes

Oxygen isotope exchange data in the brucite-water + NaCl system are summarized in Table 2. The extents of $^{18}\text{O}/^{16}\text{O}$ exchange were similar to those measured for D/H and varied from 74% after 210 days of reaction at 250°C to 97% after 14 days of reaction at 450°C (Fig. 3). Standard deviations associated with mean $10^3 \ln a_{\text{br-sw}}$ calculated by applying the partial exchange technique to successive samples vary from $+1.3\‰$ at 250°C to only $+0.2\‰$ at 450°C. Values of $10^3 \ln a_{\text{br-w}}$ are less than zero and increase slightly from 250° to 450°C (Table 2). Thus, over this temperature range, brucite is depleted in $^{18}\text{O}$ relative to coexisting NaCl solutions, and the degree of depletion decreases with increasing temperature.

Oxygen isotope fractionation factors between brucite and...
pure water have not been directly measured, but values of 1000lnα_{br-w} can be calculated from our data by considering the empirical relationship of Horita et al. (1995)

\[
10^3 \ln \Gamma^{(18)}(\text{O}) = -0.033 + 8.93 \times 10^{-7} T^2 - 2.12 \times 10^{-9} T^3
\]

that defines the effect of dissolved NaCl on \(^{18}\text{O}/^{16}\text{O}\) fractionation between two coexisting phases. This equation is directly analogous to Eqn. 6 describing the effect of dissolved NaCl on D/H fractionation and can be used with Eqn. 5 to compute values of 1000lnα_{br-w} from our measured values of 1000lnα_{m-w}. Over the temperature and salinity range of this study, \(10^3 \ln \Gamma^{(18)}(\text{O})\) values vary from \(-0.033\) to \(-0.34\)‰ in 3.0 wt% NaCl at 250°C to \(-0.34\)‰ in 10.0 wt% NaCl at 350°C (Table 2). As a consequence, 1000lnα_{br-w} values are predicted to be only slightly more positive than the corresponding values of 1000lnα_{m-w}, and still less than zero, indicating that brucite is depleted in \(^{18}\text{O}\) relative to coexisting pure water from 250° to 450°C (Fig. 5). Equation 7 was calibrated by Horita et al. (1995) to a maximum temperature of 350°C. Our application of this equation at 450°C is only meant to provide an approximation of the potential effect of dissolved salt on \(^{18}\text{O}/^{16}\text{O}\) fractionation at this condition. Moreover, because the salt-effect is predicted to be quite small in 3.0 wt% NaCl at all temperatures up to 350°C, and an order of magnitude smaller than the salt-effect on D/H fractionation, any additional uncertainty to our calculated value of 1000lnα_{br-w} introduced by extrapolating Eqn. 7 to 450°C is not likely to be significant.

The 1000lnα_{br-w} values derived in the manner described above were fit to the following equation:

\[
1000\ln \alpha_{br-w} = 9.54 \times 10^6 T^{-2} - 3.53 \times 10^4 T^{-1} + 26.58
\]

where \(T\) is temperature in Kelvins. This equation can be used to compute \(^{18}\text{O}/^{16}\text{O}\) fractionation factors between brucite and water from 250 to 450°C.

A comparison of the 1000lnα_{br-w} values determined in this study with the empirical curve for brucite-water \(^{18}\text{O}/^{16}\text{O}\) fractionation proposed by Savin and Lee (1988) shows marked disagreement in the temperature dependence from 250 to 450°C (Fig. 5). Our values increase slightly with temperature whereas the empirical predictions exhibit a sharp decrease with increasing temperature. The discrepancy is largest at 450°C (nearly 6‰) where the uncertainty associated with our experimental data is smallest (±0.2‰) because oxygen isotope exchange was close to 100%. Savin and Lee (1988) derived the fractionation curve shown in Fig. 5 from oxygen isotope exchange data for experiments in the geohite-water (Yapp, 1987) and magnetite-water (Becker, 1971; Friedman and O’Neil, 1977) systems at low temperatures and data from natural metamorphic biotite-muscovite assemblages at high temperatures. In their derivation, it was assumed that all divalent and trivalent cations bonded to OH, other than Al, have the same effect on the fractionation factor. Accordingly, the curve was designed to be applicable to all pure nonaluminous hydroxide phases. The general form of the curve is consistent with that of most common rock-forming minerals in that brucite is predicted to be enriched in \(^{18}\text{O}\) relative to coexisting pure water at low temperatures and progressively depleted in \(^{18}\text{O}\) at higher temperatures, but is inconsistent with our experimental results at high temperatures. This discrepancy with our data is likely due to large uncertainties inherent in the model-dependent assumptions that are required to derive fractionation factors for pure hydroxide phases from natural sheet-silicate assemblages. If \(^{18}\text{O}/^{16}\text{O}\) brucite-water fractionation behaves like that of most common rock-forming minerals, then we would expect the fractionation factor to become more positive at temperatures below 250°C. This would imply that 1000lnα_{br-w} reaches a minimum value at approximately 250°C, exhibiting a nonlinear temperature dependence similar to that of magnetite-water (Friedman and O’Neil, 1977). More experimental data in the brucite-water system, particularly at lower temperatures, are needed to further test this hypothesis.

3.2.1. Application of results to empirical models

Calibrations of \(^{18}\text{O}/^{16}\text{O}\) mineral-water fractionation factors have been performed by theoretical (Kieffer, 1982), semi-empirical (Zheng, 1993), and purely empirical (Savin and Lee, 1988) approaches. An important goal of these models is the prediction of fractionation factors for minerals that have not been calibrated by experiment. In the MgO-SiO_{2}-H_{2}O system, talc and serpentine, two common products of hydrothermal metamorphism, are good examples. Thus, accurate prediction of \(^{18}\text{O}/^{16}\text{O}\) fractionation factors between these minerals and water would lead to more reliable geothermometers and new constraints on the origin of metamorphic fluids.

Two calibration curves for talc and serpentine based on the models of Savin and Lee (1988) and Zheng (1993) are shown in Fig. 6. Although both models predict a decrease in 1000lnα_{m-w} values with increasing temperature, significant discrepancies exist in the magnitude and form of the temperature dependence. In particular, the Savin and Lee (1988) model predicts a more linear dependence on temperature (1/T²) and more negative 1000lnα_{m-w} values from 350° to 450°C (Fig. 6). Savin and Lee (1988) emphasize that the most uncertain aspect
of their model is the fractionation associated with divalent cations such as Mg bonded to the hydroxyl anion as in the brucite structure. Moreover, as discussed above, our 1000lnm-w values calibrated by experiment differ significantly from those predicted by Savin and Lee (1988) over the same temperature range that their model departs from that of Zheng (1993). Since brucite-like layers are an important component of talc and serpentine crystal structures, large uncertainties in the Mg-OH bond-water fractionation factor proposed by Savin and Lee (1988) could explain the discrepancies in Fig. 6. To test this possibility, the 1000lnm-br-w values determined in this study were used to calculate new oxygen isotope fractionation factors for talc and serpentine using the Savin and Lee (1988) bond-water model. For this analysis we have adopted all components of the Savin and Lee (1988) model except that we have used our 1000lnm-br-w values from 250° to 450°C in the calculation. The results show that 1000lnm m-w values in the talc-water and serpentine-water systems are displaced to more positive values from 350° to 450°C and more negative values at 250°C using our fractionation factors for brucite (Fig. 6). In effect, we predict a smaller temperature dependence than the original model of Savin and Lee (1988). Serpentine is affected more than talc as a consequence of the larger percentage of OH-bonds in the serpentine structure. For both talc and serpentine, the 1000lnm-w values determined from the modified Savin and Lee (1988) model are in excellent agreement with the calibration curve of Zheng (1993), in terms of both temperature dependence and magnitude, particularly from 350° to 450°C (Fig. 6). It is interesting to note that our experimental 1000lnm-br-w values for brucite are much more negative than those for talc or serpentine and display a very different temperature dependence (Fig. 6). This would suggest that the difference in δ18O composition of talc-brucite (Δtc-br) and serpentine-brucite (Δsp-br) pairs could be used as a geothermometer. According to the data for brucite, talc, and serpentine from this study, values of Δtc-br are 9.6, 6.8, and 4.2‰ at 250, 350, and 450°C, respectively. Corresponding values of Δsp-br are 6.4, 4.5, and 2.8‰. These data also suggest that coexisting phases in the MgO-SiO2-H2O system should exhibit the following order of enrichment with respect to 18O: talc > serpentine > brucite, consistent with the tendency for minerals rich in Si to concentrate 18O (Garlick, 1966; O’Neil and Taylor, 1967). These results should greatly enhance the accuracy of stable isotope-based models of hydrothermal processes in mafic and ultramafic systems where hydrous Mg phases are common products of fluid-rock interaction.

4. SUMMARY

Hydrogen and oxygen isotope fractionation factors between brucite and aqueous NaCl solutions (3.0-10 wt%) have been calibrated by experiment from 250 to 450°C. For hydrogen isotopes, 1000lnm-br-w values (brucite-water + NaCl system) in 3.0 wt% NaCl solutions are in good agreement with 1000lnm-sw values (brucite-water system) measured by Satake and Matsuo (1984). Thus, dissolved NaCl appears to have a small effect on D/H fractionation factors between minerals and aqueous solutions, particularly for fluids with near seawater salinity. In 10.0 wt% NaCl at 350°C, our value of 1000lnm-sw is 4‰ more positive than the corresponding value of 1000lnm-sw, suggesting that the addition of dissolved NaCl to mineral-water systems increases the amount of D fractionated into mineral structures. This result is in good agreement with other calibrations of the effect of dissolved salt on D/H fractionation between coexisting phases (Horita et al., 1995).

For oxygen isotopes, measured values of 1000lnm-br-w at 250 to 450°C indicate that brucite is depleted in 18O relative to coexisting NaCl solutions and that the degree of depletion decreases with increasing temperature and is not strongly dependent on salinity. The corresponding 1000lnm-sw values, calculated by considering the effect of dissolved salt on 18O/16O fractionation (Horita et al., 1995) were fit to the following equation:

$$1000\ln m_{sw} = 9.54 \times 10^6 T^{-2} - 3.53 \times 10^5 T^{-1} + 26.58$$

where $T$ is temperature in Kelvins. This equation is valid from 250° to 450°C and indicates that the 18O/16O brucite-water fractionation factor is significantly more negative at 250°C and more positive at 450°C, compared to values estimated by the empirical model of Savin and Lee (1988). We have modified the empirical model of Savin and Lee (1988) using our results for brucite to improve the prediction of oxygen isotope fractionation factors in the talc-water and serpentine-water systems. The resulting fractionation factors are in good agreement with those predicted using the semi-empirical/theoretical increment method of Zheng (1993). A comparison of our 18O/16O brucite-water fractionation factors with those of talc and serpentine also suggests that the δ18O composition of talc-brucite and serpentine-brucite pairs could be used as a geothermometer. These results should lead to more reliable interpretations of the δ18O composition of natural brucite, talc, and serpentine samples in hydrothermally altered mafic and ultramafic rocks.
REFERENCES


