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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 ($1000\ln\alpha_{br-sw}$) have been calibrated by experiment from 250 to 450°C at 0.5 Kb. For D/H fractionation, $1000\ln\alpha_{br-sw}$ values are as follows: $-32 \pm 6‰$ (250°C, 3.2 wt% NaCl), $-21 \pm 2‰$ (350°C, 10.0 wt% NaCl), and $-22 \pm 2‰$ (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 with 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 $^{18}O/^{16}O$ fractionation, $1000\ln\alpha_{br-sw}$ values in 3.0 wt% NaCl solutions are $-6.0 \pm 1.3‰$, $-5.6 \pm 0.7‰$ and $-4.1 \pm 0.2‰$, at 250, 350, and 450°C, respectively, and $-5.8 \pm 0.6‰$ in 10.0 wt % NaCl at 350°C. These data indicate that brucite is depleted in ^{18}O 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 $^{18}O/^{16}O$ brucite-water fractionation factors from available calibrations of the salt-effect on $^{18}O/^{16}O$ fractionation between coexisting phases. The resulting values were fit to the following equation that is valid from 250 to 450°C

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

where T is temperature in Kelvins. These new data have been used to improve the prediction of $^{18}O/^{16}O$ 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 $\delta^{18}O$ 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 ^{18}O enrichment: talc > serpentine > brucite. *Copyright © 1998 Elsevier Science Ltd*

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 salt solutions is particularly important.

Although D/H and $^{18}O/^{16}O$ fractionation factors have been determined by experiment for a large number of mineral-water pairs (O'Neil, 1986), data for minerals in the MgO-SiO$_2$-H$_2$O system are lacking. A notable example is brucite. Fractionation of ^{18}O and ^{16}O 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° to 510°C (Satake and Matsuo, 1984), but no data exists for D/H frac-

tionation in systems containing brucite and salt solutions. Moreover, empirical bond-type models have been used to calculate $^{18}O/^{16}O$ mineral-water fractionation factors for other hydrous phases in the MgO-SiO$_2$-H$_2$O 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 $^{18}O/^{16}O$ fractionation factors based on the empirical bond-water approach would be greatly improved by experimental calibration of $^{18}O/^{16}O$ 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 $^{18}O/^{16}O$ 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 $^{18}O/^{16}O$ 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

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

Days	T (°C)	NaCl wt. %	Initial fluid enriched in D				Initial fluid depleted in D				$10^3 \ln\alpha_{br-sw}$	% ex
			Wt. br grams	Wt. sw grams	δD_{br}	δD_{sw}	Wt. br grams	Wt. sw grams	δD_{br}	δD_{sw}		
0[#]	250	3.0			−74	−18			−74	−125		
27	250	3.0	0.2007	1.5316	−58	−19	0.2009	1.5178	−137	−122	−36	79.7
210	250	3.0	0.2006	1.5264	−53	−19	0.2006	1.4766	−129	−123	−28	75.6
											(−32 ± 6)	
0[#]	350	10.0			−74	−24			−74	−128		
32	350	10.0	0.2012	1.5801	−51	−25	0.2043	1.5948	−135	−126	−23	86.3
70	350	10.0	0.2061	1.5809	−49	−26	0.2003	1.5822	−131	−126	−19	84.0
225	350	10.0	0.2037	1.5886	−46	−26	0.2022	1.5838	−142	−125	−21	98.6
											(−21 ± 2)	
0[#]	450	3.0			−74	−18			−74	−125		
14	450	3.0	0.2045	1.2658	−42	−20	0.2025	1.2655	−141	−122	−23	99.5
30	450	3.0	0.2023	1.2660	−42	−20	0.2039	1.2580	−140	−122	−23	98.5
45	450	3.0	0.2056	1.2627	−38	−20	0.2013	1.2591	−142	−122	−20	103.6
											(−22 ± 2)	

* The subscripts ''br'', ''sw'', and ''w'' refer to brucite, salt-water, and pure water, respectively. Accordingly, the subscripts ''br-sw'' and ''br-w'' 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.

uncertainties associated with the use of more complex phases such as epidote in some mineral-fluid isotope exchange experiments (Horita et al., 1995). As a consequence, more studies of the effect of dissolved salt on mineral-fluid isotope fractionation are needed, particularly for compositionally and structurally simple minerals such as brucite.

In this study, D/H and $^{18}O/^{16}O$ fractionation between brucite and NaCl solutions has been investigated by experiment from 250 to 450°C at 0.5 kbar. The results provide the first experimental calibration of $^{18}O/^{16}O$ fractionation between brucite and a coexisting aqueous phase and help place constraints on the effect of dissolved salt on D/H fractionation at sub- and supercritical conditions.

2. EXPERIMENTAL

2.1. Approach

The fractionation factor between mineral and fluid ($\alpha_{mineral-fluid}$) can be defined by

$$\alpha_{\text{mineral-fluid}} = \frac{1 + \dfrac{\delta_{\text{mineral}}}{1000}}{1 + \dfrac{\delta_{\text{fluid}}}{1000}} \quad (1)$$

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

$$\delta_{\text{sample}} = \frac{R_{\text{sample}} - R_{\text{standard}}}{R_{\text{standard}}} \times 1000 \quad (2)$$

In Eqn. 2, R_{sample} and $R_{standard}$ refer to the D/H or $^{18}O/^{16}O$ 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; Suzuoki 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 depleted or enriched relative to brucite so that the brucite-fluid fractionation factor could be approached from opposite sides of the equilibrium distribution of isotopes. Calculation of equilibrium fractionation factors with this technique assumes that the extent of isotopic exchange as defined by the relationship

$$\% \text{ exchange} = \frac{\ln\alpha_i - \ln\alpha_f}{\ln\alpha_i - \ln\alpha_e} \times 100 \quad (3)$$

is equal in companion runs, where α_i, α_f, and α_e refer to the initial, final, and equilibrium value of $\alpha_{brucite-fluid}$, respectively. Thus, by equating the percentage of exchange in two companion runs, α_e can be solved from

$$\frac{\ln\alpha_{i,enr} - \ln\alpha_{f,enr}}{\ln\alpha_{i,enr} - \ln\alpha_e} = \frac{\ln\alpha_{i,dep} - \ln\alpha_{f,dep}}{\ln\alpha_{i,dep} - \ln\alpha_e} \quad (4)$$

where subscripts *enr* and *dep* refer to companion runs with initial fluids that are isotopically enriched and depleted, respectively. In principal, α_e can be calculated as a function of time and ideally the resulting values should be equivalent; that is, independent of the extent of isotopic exchange. Consequently, values of α_e 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.

2.2. Reactants

Fine-grained reagent grade $Mg(OH)_2$ was used in all experiments. X-ray diffraction (XRD) analyses indicate that this material is crystalline. Previous isotope exchange experiments in the brucite-water system 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 ^{18}O. The isotopic compositions of all reactants are given in Tables 1 and 2.

2.3. Methods

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

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 squeezed in a vice to remove air and create an initial 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 H_2 gas through reaction with U (Godfrey, 1962). The $^{18}O/^{16}O$ composition of brucite was determined by the BrF_5 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 $^{18}O/^{16}O$ composition was determined using the CO_2 equilibration approach of O'Neil et al. (1975). Analytical precision for isotope analyses were approximately ±0.1‰ and ±1.0‰ for $^{18}O/^{16}O$ 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.

3. RESULTS AND DISCUSSION

The initial fine-grained brucite underwent rapid and significant dissolution-recrystallization during all experiments. Brucite crystals could be easily observed in all reaction products, and XRD analyses showed more intense reflections compared to the starting material. Closer examination of reaction products by SEM reveals the growth of both small and large euhedral brucite crystals (Fig. 1) with the lower temperature experiments yielding a larger variation in crystal size. In general, most of the isotopic exchange during an experiment occurred prior to the first sampling occassion, a result that is consistent with rapid recrystallization of brucite during the early stages of each experiment. Thus, it is likely that isotope exchange was gov-

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

			Initial fluid enriched in ^{18}O				Initial fluid depleted in ^{18}O							
Days	T (°C)	NaCl wt. %	Wt. br grams	Wt. sw grams	$\delta^{18}O_{br}$	$\delta^{18}O_{sw}$	Wt. br grams	Wt. sw grams	$\delta^{18}O_{br}$	$\delta^{18}O_{sw}$	$10^3\ln\alpha_{br-sw}$	% ex	$10^3\ln\Gamma$	$10^3\ln\alpha_{br-w}$
0#	250	3.0			−3.4	22.6			−3.4	−53.0				
27	250	3.0	0.2007	1.5316	7.8	21.7	0.2009	1.5178	−37.0	−50.2	−6.9	64.3	−0.05	−6.9
210	250	3.0	0.2006	1.5264	10.7	21.4	0.2006	1.4766	−40.6	−49.8	−5.1	73.7	−0.05	−5.1
											(−6.0 ± 1.3)		−0.05	(−6.0 ± 1.3)
0#	350	3.0			−3.4	22.6			−3.4	−53.0				
31	350	3.0	0.2004	1.5208	11.8	21.3	0.2001	1.5301	−44.1	−49.6	−5.3	80.3	−0.11	−5.2
79	350	3.0	0.2004	1.4384	11.3	21.3	0.2005	1.5310	−46.0	−49.4	−6.5	82.5	−0.11	−6.4
128	350	3.0	0.2006	1.5197	12.6	21.3	0.2005	1.5086	−45.1	−49.5	−5.0	82.9	−0.11	−4.9
223	350	3.0	0.2009	1.5320	12.7	21.3	0.2006	1.5173	−46.7	−49.4	−5.5	85.4	−0.11	−5.4
											(−5.6 ± 0.7)		−0.11	(−5.5 ± 0.7)
0#	450	3.0			−3.4	22.6			−3.4	−53.0				
14	450	3.0	0.2045	1.2658	15.9	20.6	0.2025	1.2655	−50.5	−48.2	−4.0	97.1	−0.2	−3.8
30	450	3.0	0.2023	1.2660	15.4	20.7	0.2039	1.2580	−49.6	−48.3	−4.1	95.1	−0.2	−3.9
45	450	3.0	0.2056	1.2627	15.7	20.6	0.2013	1.2591	−50.8	−48.2	−4.3	97.3	−0.2	−4.1
											(−4.1 ± 0.2)		−0.2	(−3.9 ± 0.2)
0#	350	10.0			−3.4	22.6			−3.4	−53.0				
32	350	10.0	0.2012	1.5801	7.9	21.6	0.2043	1.5948	−35.1	−50.2	−6.0	61.8	−0.34	−5.7
70	350	10.0	0.2061	1.5809	8.9	21.5	0.2003	1.5822	−36.0	−50.2	−5.1	64.6	−0.34	−4.8
225	350	10.0	0.2037	1.5886	10.2	21.4	0.2022	1.5838	−42.0	−49.6	−6.2	75.2	−0.34	−5.9
											(−5.8 ± 0.6)		−0.34	(−5.5 ± 0.6)

* The subscripts ''br'', ''sw'', and ''w'' refer to brucite, salt-water, and pure water, respectively. Accordingly, the subscripts ''br-sw'' and ''br-w'' 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.
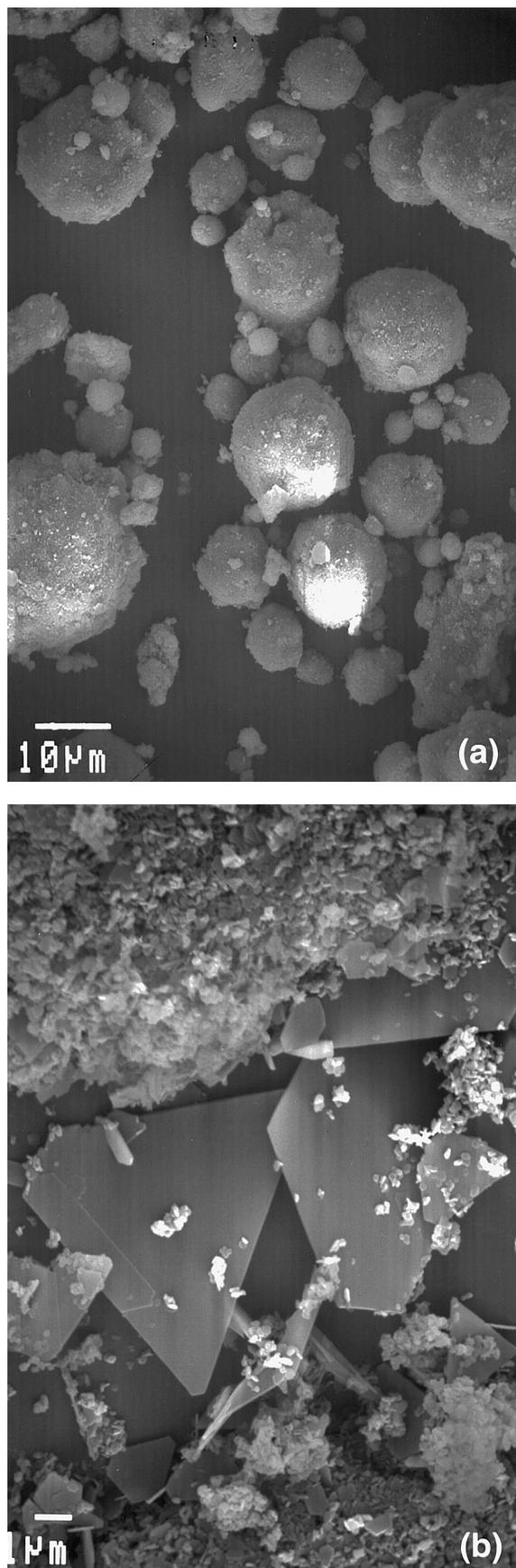
erned primarily by dissolution-recrystallization, rather than volume diffusion. Moreover, at each temperature the extent of D/H exchange between brucite and the NaCl fluid was similar to the extent of $^{18}O/^{16}O$ exchange (Figs. 2 and 3). These data are consistent with a dissolution-recrystallization 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 α_e were computed as a function of time for each experiment. Because the extent of isotope exchange increased only slightly after the first sampling occassion in most experiments, we adopted the mean α_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 ±6‰ at 250°C to ±2‰ 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 (Γ) on mineral-water fractionation factors for any pair of stable isotopes can be written as

$$10^3\ln \Gamma = 10^3\ln \alpha_{m-sw} - 10^3\ln \alpha_{m-w} \qquad (5)$$

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

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.
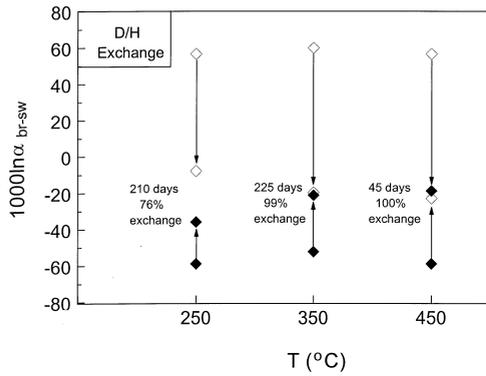
Fig. 2. Changes in $1000\ln\alpha_{br-sw}$ with time for D/H exchange at 250 to 450°C. Arrows indicate the progression of $1000\ln\alpha_{br-sw}$ values from the initial condition to the final sample for companion capsules.

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 $10^3\ln\alpha_{br-sw}$ appears to be more positive than the corresponding value of $10^3\ln\alpha_{br-w}$ 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 $10^3\ln\Gamma$ value of +4‰ 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 + NaCl system and derived the following empirical relationship:

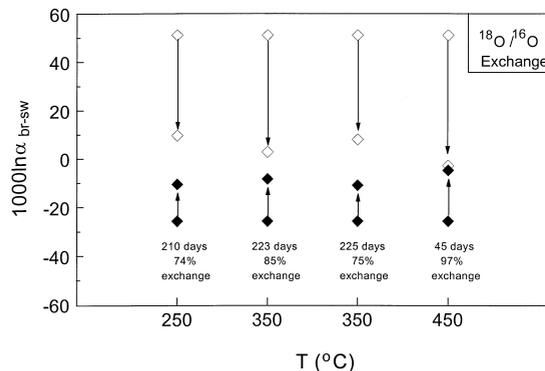$$10^3\ln\Gamma(D) = m(0.01680T - 13.79 + 3255/T) \quad (6)$$

Fig. 3. Changes in $1000\ln\alpha_{br-sw}$ with time for $^{18}O/^{16}O$ exchange at 250 to 450°C. Arrows indicate the progression of $1000\ln\alpha_{br-sw}$ values from the initial condition to the final sample for companion capsules. The extents of isotopic exchange shown here are similar to those accompanying D/H exchange.

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‰) 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 can not statistically constrain a precise value for Γ 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 Γ 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 $^{18}O/^{16}O$ 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 $1000\ln\alpha_{br-sw}$ 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 $1000\ln\alpha_{br-w}$ are less than zero and increase slightly from 250° to 450°C (Table 2). Thus, over this temperature range, brucite is depleted in ^{18}O relative to coexisting NaCl solutions, and the degree of depletion decreases with increasing temperature.
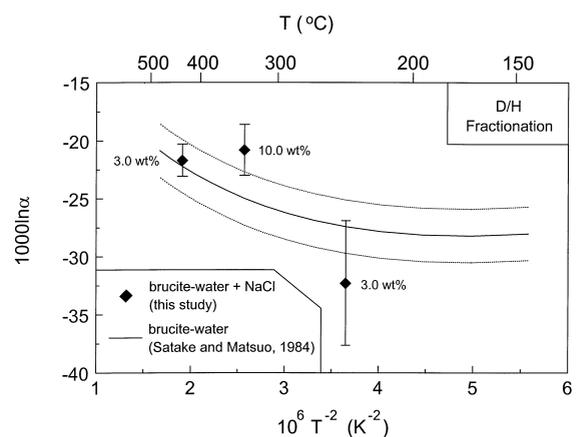
Oxygen isotope fractionation factors between brucite and

Fig. 4. Comparison of $1000\ln\alpha$ values for D/H fractionation in the brucite-water and brucite-water+NaCl systems. The dotted lines show the ±2.3‰ standard deviation associated with the data of Satake and Matsuo (1984). Based on this analysis, the salt-effect appears to be small (within the error of the fractionation factors) for fluids with near seawater salinity (3.0 wt% NaCl). At 10.0 wt% NaCl, the $1000\ln\alpha$ value appears to be more positive than the value in pure water, suggesting that the addition of salt increases the amount of deuterium fractionated into mineral structures.

pure water have not been directly measured, but values of $1000\ln\alpha_{br-sw}$ can be calculated from our data by considering the empirical relationship of Horita et al. (1995)

$$10^3\ln\Gamma(^{18}O) =$$
$$m(-0.033 + 8.93 \times 10^{-7}T^2 - 2.12 \times 10^{-9}T^3) \quad (7)$$

that defines the effect of dissolved NaCl on $^{18}O/^{16}O$ 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 $1000\ln\alpha_{br-w}$ from our measured values of $1000\ln\alpha_{br-sw}$. Over the temperature and salinity range of this study, $10^3\ln\Gamma(^{18}O)$ values vary from -0.05‰ in 3.0 wt% NaCl at 250°C to -0.34‰ in 10.0 wt% NaCl at 350°C (Table 2). As a consequence, $1000\ln\alpha_{br-w}$ values are predicted to be only slightly more positive than the corresponding values of $1000\ln\alpha_{br-sw}$ and still less than zero, indicating that brucite is depleted in ^{18}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 $^{18}O/^{16}O$ 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 $1000\ln\alpha_{br-w}$ introduced by extrapolating Eqn. 7 to 450°C is not likely to be significant.

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

$$1000\ln\alpha_{br-w} = 9.54 \times 10^6 T^{-2} - 3.53 \times 10^4 T^{-1} + 26.58 \quad (8)$$

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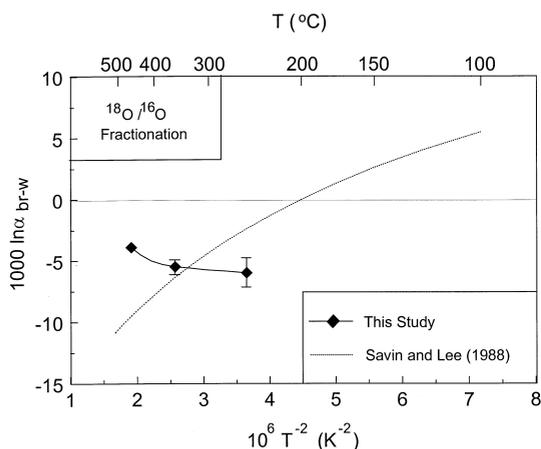

Fig. 5. A comparison of $1000\ln\alpha_{br-sw}$ values for $^{18}O/^{16}O$ fractionation measured in this study with those predicted by the empirical model of Savin and Lee (1988). The experimental data indicate that $1000\ln\alpha_{br-sw}$ increases slightly with temperature whereas the empirical predictions show the opposite trend with $1000\ln\alpha_{br-sw}$ decreasing with increasing temperature.

A comparison of the $1000\ln\alpha_{br-w}$ values determined in this study with the empirical curve for brucite-water $^{18}O/^{16}O$ 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 geothite-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}O relative to coexisting pure water at low temperatures and progressively depleted in ^{18}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 $^{18}O/^{16}O$ 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 $1000\ln\alpha_{br-w}$ 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 $^{18}O/^{16}O$ 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 $^{18}O/^{16}O$ 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 $1000\ln\alpha_{m-w}$ 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 ($1/T^2$) and more negative $1000\ln\alpha_{m-w}$ values from 350° to 450°C (Fig. 6). Savin and Lee (1988) emphasize that the most uncertain aspect
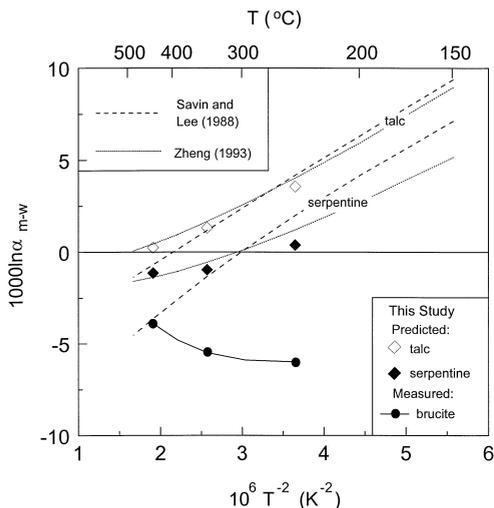
Fig. 6. A comparison of $1000\ln\alpha_{m-w}$ values for ^{18}O-^{16}O fractionation in the talc-water and serpentine-water systems as predicted by empirical and semi-empirical models. We have incorporated the $1000\ln\alpha_{br-w}$ values calibrated in this study by experiment into the Savin and Lee (1988) model from 250 to 450°C. The empirical predictions modified in this manner (diamonds) are in much better agreement with the semi-empirical increment model of Zheng (1993). This analysis also shows that brucite should be strongly depleted in ^{18}O when coexisting with talc or serpentine and that talc-brucite and serpentine-brucite pairs could be used as a geothermometer.

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 $1000\ln\alpha_{br-w}$ 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 the 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 $1000\ln\alpha_{br-w}$ 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 $1000\ln\alpha_{br-w}$ values from 250° to 450°C in the calculation. The results show that $1000\ln\alpha_{m-w}$ 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 $1000\ln\alpha_{m-w}$ 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 $1000\ln\alpha_{m-w}$ 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 $\delta^{18}O$ composition of talc-brucite (Δ_{tc-br}) and serpentine-brucite (Δ_{sp-br}) pairs could be used as a geothermometer. According to the data for brucite, talc, and serpentine from this study, values of Δ_{tc-br} are 9.6, 6.8, and 4.2‰ at 250, 350, and 450°C, respectively. Corresponding values of Δ_{sp-br} are 6.4, 4.5, and 2.8‰. These data also suggest that coexisting phases in the MgO-SiO_2-H_2O system should exhibit the following order of enrichment with respect to ^{18}O: talc > serpentine > brucite, consistent with the tendency for minerals rich in Si to concentrate ^{18}O (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, $1000\ln\alpha_{br-sw}$ values (brucite-water + NaCl system) in 3.0 wt% NaCl solutions are in good agreement with $1000\ln\alpha_{br-w}$ 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 $1000\ln\alpha_{br-sw}$ is 4‰ more positive than the corresponding value of $1000\ln\alpha_{br-w}$, 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 $1000\ln\alpha_{br-sw}$ at 250 to 450°C indicate that brucite is depleted in ^{18}O relative to coexisting NaCl solutions and that the degree of depletion decreases with increasing temperature and is not strongly dependent on salinity. The corresponding $1000\ln\alpha_{br-w}$ values, calculated by considering the effect of dissolved salt on ^{18}O/^{16}O fractionation (Horita et al., 1995) 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 is valid from 250° to 450°C and indicates that the ^{18}O/^{16}O 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 ^{18}O/^{16}O brucite-water fractionation factors with those of talc and serpentine also suggests that the $\delta^{18}O$ composition of talc-brucite and serpentine-brucite pairs could be used as a geothermometer. These results should lead to more reliable interpretations of the $\delta^{18}O$ composition of natural brucite, talc, and serpentine samples in hydrothermally altered mafic and ultramafic rocks.

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