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4 **Oxygen isotope fractionation in the portlandite-water and brucite-water systems from 125° to**
5 **450°C, 50 MPa**
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ABSTRACT

Equilibrium oxygen isotope fractionation factors were determined for the portlandite-water and brucite-water systems from 125 to 425°C, 50 MPa using the partial exchange technique. Reagent grade cryptocrystalline $\text{Ca}(\text{OH})_2$ and amorphous $\text{Mg}(\text{OH})_2$ were reacted with three waters having different initial $\delta^{18}\text{O}$ compositions. Isotope exchange occurred via recrystallization with exchange varying from 40 to 95% at 200 to 425°C, respectively. Equilibrium ^{18}O brucite-water fractionation factors ($10^3 \ln \alpha$) increase from $-4.7 \pm 3.5\text{‰}$ at 200°C to $-3.5 \pm 2.5\text{‰}$ at 425°C. These data connect smoothly with previous experimental calibrations at lower and higher temperatures to define a single function valid from 15 to 450°C, as follows:

$$10^3 \ln \alpha_{\text{brucite-water}} = 4.39 \times \frac{10^6}{T^2} - 16.95 \times \frac{10^3}{T} + 11.19$$

where T is temperature in Kelvin. These results confirm the existence of a broad minimum in the fractionation factor for brucite at $\sim 250^\circ\text{C}$. The equilibrium ^{18}O fractionation factor for portlandite-water varies from $-11.1 \pm 2.7\text{‰}$ at 125°C to $-6.6 \pm 0.1\text{‰}$ at 425°C, and can be described by the following function:

$$10^3 \ln \alpha_{\text{portlandite-water}} = 5.61 \times \frac{10^6}{T^2} - 26.29 \times \frac{10^3}{T} + 19.72$$

where T is temperature in Kelvin. These experimental results indicate that brucite favors ^{18}O relative to portlandite with brucite-portlandite fractionation decreasing from 8 to 3‰ from 125 to 425°C. A significant temperature dependent cation mass effect is therefore indicated for cation-OH bonds in hydroxide minerals. The observed fractionation is consistent with quantum theory which predicts that bonds with less massive cations have higher vibrational frequencies and will display a relative affinity for ^{18}O to stabilize the structure. Brucite-portlandite ^{18}O fractionation predicted using the increment method is extremely small, opposite in sign (-0.1 to -0.2‰), and shows very little dependence on temperature, in poor agreement with the experimental calibration. This indicates that the method does not adequately account for the effect of cation mass on ^{18}O fractionation within hydroxide minerals. It is suggested that cation-specific parameters within the increment method could be fit to the experimental calibrations reported here to improve prediction of fractionation factors for hydroxides and hydroxyl-bearing aluminosilicates, particularly at low temperature where the cation-mass effect is more significant.

1. INTRODUCTION

Equilibrium oxygen isotope fractionation factors between hydroxide minerals and water have been determined using a variety of approaches over a range of temperature and pressure conditions. This includes calibration from laboratory experiments, natural samples, and semi-empirical predictions based on correlations between bond strength and the degree of ^{18}O enrichment in minerals. Laboratory experiments have been conducted in the $\text{Al}(\text{OH})_3$ (gibbsite)-water system from 0-60°C (Bird et al., 1994; Vitali et al., 2000), the $\text{FeO}(\text{OH})$ (goethite)-water system from 10-140°C (Yapp, 1987; 1990; Muller, 1995; Bao and Koch, 1999), and the $\text{Mg}(\text{OH})_2$ (brucite)-water system from 15-120°C (Xu and Zheng, 1999) and 250-450°C (Saccocia et al., 1998). The low temperature experiments (<140°C) utilized different reactions to precipitate the hydroxide phase in solution whereas the higher temperature experiments of Saccocia et al. (1998) involved recrystallization of amorphous $\text{Mg}(\text{OH})_2$. For goethite the magnitude of laboratory-based fractionation factors using different reactions is highly discrepant, a result that may be attributed to a lack of isotopic equilibrium and difficulties encountered when working with very fine grained Fe-bearing precipitates containing adsorbed water (Chacko et al., 2001). For the brucite-water system, Xu and Zheng (1999) report consistent fractionation factors from three different synthesis reactions and argue that this agreement supports the assumption that isotopic equilibrium was reached.

Collectively, low temperature data from these laboratory experiments suggest that ^{18}O mineral-water fractionation for all hydroxide phases have a similar temperature dependency, with values decreasing with increasing temperature up to 140°C. The low temperature fractionation curve of Xu and Zheng (1999), taken together with the high temperature results of Saccocia et al. (1998) that show an increase in the fractionation factor from 250 to 450°C,

suggests that the brucite-water fractionation factor reaches a minimum in the vicinity of 200°C. There is no other fractionation data at temperatures >200°C from experiments to confirm if this complex temperature dependency is common to other pure hydroxide phases.

Semi-empirical calibration techniques offer a way to compute equilibrium oxygen isotope fractionation factors for mineral-water systems and temperature conditions where experimental data are lacking or difficult to obtain. These techniques are based on the observation that the degree of ^{18}O enrichment in minerals is correlated to cation-oxygen bond strength (Taylor and Epstein, 1962; Garlick, 1966). Such models typically rely on experimental data or data from natural samples as a reference to compute fractionation factors. Thus, the predictions represent equilibrium values insofar as the fractionation data used to calibrate the model represent the equilibrium condition.

Using the $\delta^{18}\text{O}$ composition of quartz, anorthite, and olivine within igneous rocks, Taylor and Epstein (1962) assigned ^{18}O fractionation values to Si-O-Si, Si-O-Al, and Si-O-M $^{2+}$ bonds and proposed that fractionation factors for other silicates could be computed by summing the fractionation assigned to each of these three bond types within a mineral. Savin and Lee (1988) modified this approach for OH-bearing minerals by considering oxygen isotope exchange experiments in the goethite-water system at low temperatures (Yap, 1987), along with data from natural metamorphic biotite-muscovite assemblages at high temperatures (Bottinga and Javoy, 1975). In their formulation, Savin and Lee (1988) assumed that all divalent and trivalent cations bonded to OH other than Al have the same effect on oxygen isotope fractionation. This assumption is inconsistent with experimental evidence at low temperature suggesting a different fractionation for OH bonded to Fe $^{3+}$ and Mg $^{2+}$ (Xu and Zheng, 1999). Moreover, there is poor agreement between the Savin and Lee (1988) fractionation curve for brucite and experimental

calibrations (Saccocia et al. 1998; Xu and Zheng, 1999). Notably, the Savin and Lee (1988) brucite-water fractionation curve decreases with increasing temperature to 500°C and does not capture the minimum suggested by experimental data at approximately 200°C.

The increment method is another semi-empirical approach to compute oxygen isotope fractionation between minerals and water. In this approach originally developed by Schütze (1980) and applied to silicate minerals by Richter and Hoernes (1988), ^{18}O increment values for cation-oxygen bonds are computed by considering bond strength and length in addition to cation mass, valence, and coordination number. These increment values are then used to calculate an ^{18}O index for a mineral by summing the ^{18}O increments for different cation-oxygen bonds in the mineral structure using the Si-O bond as a reference. The ^{18}O index establishes a mineral's propensity to incorporate ^{18}O into the structure relative to quartz. To compute absolute fractionation factors, the ^{18}O index can be linked to the reduced partition function ratios of quartz which were originally calculated by Kieffer (1982) and adjusted by Clayton et al. (1989). The increment method was modified by Zheng (1991, 1993a, b) for application to metal oxides, anhydrous silicates and hydroxyl-bearing silicates. Zheng (1998) extended the technique to include hydroxide minerals.

A comparison of oxygen isotope fractionation factors derived from experiment with those predicted using the increment method show generally good agreement for anhydrous silicates. Similar comparisons for oxides and hydrous silicates, however, suggest that the method might not adequately account for the effect of cation mass and the presence of hydroxyl groups on the relative affinity for ^{18}O (Chacko et al, 2001), highlighting the need for laboratory calibration experiments. It is notable that the oxygen isotope fractionation curve for the brucite-water system computed from the increment method (Zheng, 1998) is in good agreement with the low

temperature experimental calibration of Xu and Zheng, (1999). It also predicts a minimum from 300-375°C which is in broad agreement with the experimental results of Saccocia et al. (1998) although the experimentally derived fractionation factors are 2‰ more positive than the empirical results at 450°C and suggest that the minimum occurs over a narrower and lower temperature range. Thus, a major goal of the present study is to experimentally derive oxygen isotope brucite-water fractionation factors at new temperature points from 200 to 425°C to confirm and refine the minimum suggested by prior experiments and better anchor the higher temperature portion of the fractionation curve. The results have broad implications for understanding natural occurrences of brucite, a common mineral associated with diverse geologic processes including metamorphism of carbonate rocks (Ferry et al, 2010), serpentinization of ultramafic rocks (Wenner and Taylor, 1971; 1974), and hydrothermal chimney formation on the seafloor (Ludwig et al, 2006). These processes occur over a temperature range that includes the minimum in the brucite-water fractionation curve indicated by existing experimental data.

The present study also provides the first experimental calibration of oxygen isotope fractionation between portlandite ($\text{Ca}(\text{OH})_2$) and water. Portlandite is a rare mineral associated with diverse geologic settings including veins formed from alkaline solutions hosted by impure limestones (Kolodny et al, 2014) and serpentinized ultramafic rocks (Neal and Stanger, 1984), regions of contact metamorphism within organic rich marls and limestones (Saines et al, 1980), miarolitic cavities hosted by granite pegmatites (Birch, 1996), and carbonatite complexes (Reid and Cooper, 1992). Our particular interest is in how the fractionation factor for portlandite compares to that of brucite given their similar structure and the large mass difference between Ca and Mg. Thus, the results of this study pertain specifically to Mg-OH and Ca-OH bonding in

minerals and therefore provide an experimental basis for refinement of semi-empirical models that consider cation mass to predict ^{18}O fractionation in OH-bearing minerals. Stable isotope theory suggests that ^{18}O should form a stronger bond and be more enriched in phases with higher bond stiffness, which increases for elements with a smaller mass (Urey, 1947; Bigeleisen and Mayer, 1947; see also review by Sharp, 2007). These relationships suggest that brucite should incorporate more ^{18}O into its structure relative to portlandite, a conclusion that is tested by the new data presented here. It is noteworthy that the increment model proposed by Zheng (1998) for hydroxide phases predicts the opposite with portlandite being slightly enriched in ^{18}O compared to brucite although the difference between the two is small ($<0.2\%$). Moreover, Zheng (1998) also predicts that the portlandite-water fractionation factor has a broad minimum from 300-375°C, suggesting a complex temperature dependency similar to that of brucite. The present study tests these predictions by experimentally calibrating the portlandite-water fractionation factor from 125 to 425°C.

2. EXPERIMENTAL

2.1. Approach

The mineral-water fractionation factor (α) is defined by the expression:

$$\alpha = \frac{1 + \frac{\delta_{\text{mineral}}}{1000}}{1 + \frac{\delta_{\text{water}}}{1000}} \quad (1)$$

where δ_{mineral} and δ_{water} refer to the isotopic composition of coexisting mineral-water pairs in standard delta notation as follows:

$$\delta_{sample} = \frac{\left(\frac{O^{18}}{O^{16}}\right)_{sample} - \left(\frac{O^{18}}{O^{16}}\right)_{standard}}{\left(\frac{O^{18}}{O^{16}}\right)_{standard}} \times 1000 \quad (2)$$

In this study, all δ values are reported in units of per mil (‰) relative to VSMOW.

The partial exchange technique (Northrop and Clayton, 1966; Suzuoki and Epstein, 1976; O’Neil, 1986) was employed to determine equilibrium ^{18}O fractionation factors for brucite and portlandite. The experimental approach used by Saccocia et al. (1998; 2009) was modified to include three companion runs that are identical in every respect except for the initial fluids that were characterized by enriched, depleted, or intermediate ^{18}O values relative to the starting solid.

The extent of isotope exchange between a mineral-water pair during an experiment can be defined by the expression:

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

where α_i , α_f , and α_e are the initial, final, and equilibrium value of $\alpha_{\text{mineral-water}}$ respectively (O’Neil, 1986). In this equation, the % exchange is the extent to which the initial distribution of isotopes between the solid and water on a mole basis has reached the distribution at equilibrium. Values of α_i are known from the measured $\delta^{18}\text{O}$ of the initial solid and fluid reactants. Values of α_f can be computed from measured changes in $\delta^{18}\text{O}$ of the mineral during an experiment together with a material balance calculation to determine the isotopic composition of the water. If it is assumed that the % exchange for any two companion runs is the same, then equation (3) can be equated for each run and solved for α_e .

2.2. Starting Material

Reagent grade amorphous $\text{Mg}(\text{OH})_2$ and cryptocrystalline $\text{Ca}(\text{OH})_2$ with a purity of 99.9% was used in the experiments (Fig. 1A, B). Both brucite and portlandite are stable phases in aqueous systems at the temperature-pressure conditions explored here (Meyer and Yang, 1962, Bai et al., 1994). The initial $\delta^{18}\text{O}$ values for brucite and portlandite were -2.9‰ and 7.9‰ respectively. Three isotopically distinct starting waters were prepared using deionized water spiked with ^{16}O and ^{18}O to achieve initial $\delta^{18}\text{O}$ values of 52.3, -7.3, and -49.7‰. This combination of starting compositions resulted in a large range of initial mineral-water fractionation ($10^3 \ln \alpha_i$) that varied from -53.9 to 48.1‰ for brucite and -43.1 to 58.9‰ for portlandite (Tables 1 and 2).

Fluid/solid mass ratios varied from 6.25-7.50 for the portlandite runs and 6.8-7.5 for the brucite runs, with the lower ratios deployed at 425°C to account for greater fluid expansion at that condition. These mass ratios correspond to fluid/solid mole ratios for oxygen of 12.8-15.4 and 11.2-12.2 for portlandite and brucite runs, respectively. The initial fluid is undersaturated with mineral reactants, which drives dissolution during the early stages of an experiment. Brucite and portlandite solubility decreases with increasing temperature (Walther, 1986; Seewald and Seyfried, 1991), so the amount of dissolution would be greatest for the low temperature experiments. Solubility calculations indicate that for portlandite at 125°C, 7.4×10^{-4} grams will dissolve to reach saturation, which is 0.37% of the initial solid charge. Because of the substantially greater amount of oxygen in the fluid, this dissolution will change the $\delta^{18}\text{O}$ of the initially enriched and depleted fluid by only 0.01‰. The effect is less for the intermediate fluid which has a $\delta^{18}\text{O}$ composition closer to that of the initial portlandite. For brucite at 200°C, 3.7×10^{-6} grams will dissolve, which represents 0.002% of the initial solid charge. This will change the $\delta^{18}\text{O}$ of the initial fluids by 0.001‰ or less.

During the course of each experiment the potential exists for mineral zonation during recrystallization of the solid charge. This could occur if the isotopic composition of the fluid shifts during progressive recrystallization. Such a shift would, in turn, shift the isotopic composition of newly formed crystals. In the experimental approach deployed here, we measure the bulk isotopic composition of the solid charge after reaction and compute the corresponding bulk isotopic composition of the fluid from a material balance. With this approach, α_e values calculated using equation (3) are not affected by zonation as long as each increment of recrystallized solid formed is in isotopic equilibrium with the coexisting water and the effect is identical in companion runs. Mineral zonation would, however, introduce errors for values of percent exchange calculated from equation (3). If it is assumed that each increment of recrystallized solid formed does not re-equilibrate with the fluid during continued reaction to maintain isotopic zonation, the calculated percent exchange reported in Tables 1 and 2 would underestimate the actual values by a maximum of 5% for the experimental run conditions deployed here.

2.3. Methods

Experiments were performed using flexible gold capsules (1 cm o.d., 0.13 mm wall thickness, 5 cm length, 4 ml internal volume) contained within steel pressure vessels. Each capsule was welded at one end prior to loading with the initial solid and fluid reactants. After loading the solid and fluid reactants, the capsule headspace was sparged with helium gas to remove air before the open end was squeezed in a vice to create an initial seal. This seal was then welded while the bottom end of the capsule containing the reactants was submerged in liquid nitrogen to prevent heating of the capsule contents. The weight of the sealed capsule was

compared to the weight of the unsealed gold capsule plus the fluid and solid reactants. Sealed capsules that differed from the initial weight (before welding) by more than 0.1% were discarded.

Six gold capsules containing identical solid reactants were prepared for each mineral-water system investigated at a given temperature. Three capsules with different initial fluids (enriched, depleted, and intermediate) were placed in one pressure vessel and the other three identical capsules were placed in a second pressure vessel. Both pressure vessels were then loaded into a single tube furnace. The internal pressure of each gold capsule was monitored using a thin-filmed pressure transducer and externally controlled at 50 MPa by pumping water into the pressure vessels. Temperature was monitored by a thermocouple inserted into a well that extended into the pressure fluid surrounding the gold capsules at the back end of each pressure vessel. To monitor temperature gradients, two additional thermocouples were attached along the exterior wall of each pressure vessel. The tube furnace containing the pressure vessels was heated to the desired temperature in less than 2 hours while bleeding off excess pressure fluid. Using this apparatus, the temperature of each pressure vessel was controlled to $\pm 2^{\circ}\text{C}$. Thermal gradients along the length of the each pressure vessel were less than 2°C .

Reaction progress was determined by removing one pressure vessel from the tube furnace at two different time intervals. Reaction times varied from 7 to 148 days depending on temperature. During sampling, each pressure vessel was cooled to room temperature in less than 10 minutes by exposure to a cold gas stream followed by immersion in a chilled water bath. The capsules were then immediately removed, cleaned, and weighed to confirm that capsule mass remained constant during the experiment. Each capsule was then opened to remove the solid products which were dried at 40°C prior to isotopic analyses and mineralogical characterization

by X-Ray diffraction (XRD) and scanning electron microscopy (SEM). Because the solubility of brucite and portlandite increases with decreasing temperature (Walther, 1986; Seewald and Seyfried, 1991) precipitation of solids during sampling related cooling could not occur. Moreover, this increase in solubility at low temperature decreases the thermodynamic drive to recrystallize new solid making continued isotope exchange during cooling unlikely. The maximum amount of dissolution that can occur during cooling is defined by the change in brucite and portlandite solubility from the run temperature to 25°C. For portlandite cooling from 300°C, for example, 2.4×10^{-5} moles (0.0018 grams) would dissolve assuming dissolution is rapid enough for the solution to reach equilibrium during the 10 minute quench process. This would shift the $\delta^{18}\text{O}$ of the solution by only 0.01‰. For brucite cooling from the same temperature, the effect is even smaller with only 1.1×10^{-7} moles (6.4×10^{-6} grams) brucite dissolving shifting the $\delta^{18}\text{O}$ of the fluid by only 0.001‰.

Isotopic analyses were performed at the USGS in Denver using a Finnigan Mat 252 mass spectrometer. The oxygen isotopic composition of the solids was determined by the BrF_5 technique (Clayton and Mayeda, 1963). For the initial waters, $\delta^{18}\text{O}$ values were determined using the CO_2 equilibration method of O'Neil et al. (1975). Analytical precision for oxygen isotope analyses was $\pm 0.2\text{‰}$ based on replicate analyses of the standard. Because the experiments were conducted in a closed system with large fluid/solid mole ratios for oxygen, the isotopic composition of the fluid after reaction was calculated by material balance using the large measured changes in the isotopic composition of the solid phases.

3. RESULTS AND DISCUSSION

3.1. Overview

During the course of the experiments involving the brucite-water and portlandite-water systems, large changes in the $\delta^{18}\text{O}$ of the solid charge were measured (Tables 1 and 2) and significant recrystallization was observed from SEM analyses (Figs. 1C-F). The amount of exchange calculated using equation (3) increased with time and temperature, varying from 40 to 94% from 200 to 425°C for brucite, and 54 to 95% from 125 to 425°C for portlandite. The rate that ^{18}O mineral-water fractionations converge increased with temperature (Figs. 2 and 3) which is an important variable that governs recrystallization rates (Cole and Chakraborty, 2001).

In an isotope exchange experiment between mineral and water where lattice diffusion is the primary exchange mechanism, equilibrium can be confirmed from multiple experiments with distinct initial $\delta^{18}\text{O}$ compositions. As exchange proceeds, the ^{18}O mineral-water fractionation factor converges on a single value from opposite directions relative to the equilibrium distribution of isotopes. This experimental design is often referred to as the two-direction method and is most successfully applied at temperatures above 550°C where lattice diffusion rates are rapid (O'Neil, 1986). In the experiments conducted here at lower temperature, recrystallization and isotope exchange occurs via Ostwald ripening whereby dissolution of an initially amorphous or cryptocrystalline solid is followed by precipitation of larger euhedral crystals 10-20 μm in diameter (Fig. 1C-F). These larger crystals may form by homogenous precipitation from solution at new nucleation sites or by growth on smaller grains. Because this process involves mass transfer of oxygen isotopes through the aqueous phase, isotope exchange between the solid charge and water proceeds from only one direction, despite large differences in the initial ^{18}O mineral-water fractionation in companion runs that brackets the inferred equilibrium distribution of isotopes. Thus, the observed convergence of ^{18}O mineral-water fractionation with time (Figs.

2 and 3) does not constitute proof that isotopic equilibrium is being approached or has been achieved, as it does in the two-direction method when lattice diffusion is the dominant exchange mechanism. Thus, we cannot unequivocally preclude kinetic effects as a control on the observed fractionation during the present study and must assume that the fractionation factors calculated using equation (3) above are equilibrium values. Because the recrystallization rate decreases with time as Ostwald ripening proceeds and crystal size increases, we might expect α_e values calculated from equation (3) to vary systematically with time if kinetic effects are controlling the fractionation. We do not observe such patterns in the present investigation, consistent with our assumption that equilibrium controls the fractionation.

Because we adopted three different initial fluid compositions that were sampled on two occasions for both the brucite and portlandite experiments, six equilibrium fractionation factor (α_e) values were calculated using equation (3) for each mineral-water system at a given temperature (Tables 1 and 2). Any variation in these α_e values reflects experimental and analytical errors as well as uncertainties associated with the assumption that the % exchange in companion runs is equal. The overall equilibrium fractionation factors and standard deviations reported here for brucite and portlandite (Table 3) were calculated from the six values determined at each temperature. The standard deviations do not include uncertainties that could arise if kinetic effects partially or in total control the observed fractionation.

3.2. Brucite-water

For the brucite-water system, the equilibrium fractionation factor varies from -4.7 to -3.5‰ from 200-425°C (Fig. 4) consistent with the results of Saccocia et al. (1998) from 250-450°C. This result indicates that brucite incorporates less ^{18}O into its structure relative to coexisting

water, but becomes progressively more ^{18}O rich with increasing temperature. Experimental calibration of brucite-water fractionation at lower temperatures (Xu and Zheng, 1999) indicates that the fractionation factor decreases with increasing temperature from 15 to 120°C and exhibits a crossover from positive to negative values at 60°C. These data smoothly connect with the measured values from this study and the earlier results of Saccocia et al (1998). All of these experimental results can be described by the single relationship:

$$10^3 \ln \alpha_{\text{brucite-water}} = 4.39 \times \frac{10^6}{T^2} - 16.95 \times \frac{10^3}{T} + 11.19 \quad (4)$$

where T is temperature in Kelvin. Equation (4) is valid for the experimentally calibrated range from 15 to 450°C and confirms that the oxygen isotope fractionation factor for the brucite-water system reaches a broad minimum at ~250°C (Fig. 4).

A comparison of the brucite-water fractionation factor with that for hydrous magnesium silicates calibrated from laboratory experiments reveals that the relative extent of ^{18}O enrichment for each of the minerals is consistent with stable isotope theory (Fig. 5). Brucite is the most depleted in ^{18}O whereas talc is the most enriched relative to the other phases. This same pattern of ^{18}O enrichment is predicted by the increment method (Zheng, 1993b; 1998). Mineral structures that are dominated by bonds with higher vibrational frequency generally have a greater affinity for ^{18}O . However, the vibrational frequency shift upon isotopic substitution is also a critical factor and this tends to dominate at lower temperatures (Urey, 1947). Thus, isotopic substitutions associated with a larger decrease in vibrational frequency will be favored. The frequency shift associated with ^{18}O substitution into the O-H bond is significantly less than that for the Si-O and Al-O bonds and as a consequence the hydroxyl group favors ^{16}O relative to aluminosilicate oxygen (O'Neil, 1986). Thus, pure hydroxide phases such as brucite are most depleted in ^{18}O whereas hydrous silicates with proportionally more Si-O bonds such as talc are

the most enriched. Brucite is also the only phase shown that exhibits a minimum in the fractionation factor, becoming more enriched in ^{18}O with increasing temperature from 250 to 450°C (Fig. 5). This is also a likely consequence of the absence of Si-O bonding in the brucite structure. Quartz-water fractionation over this same temperature range exhibits a decrease of approximately 6‰ (Matsuhisa et al. 1979) indicating that fractionation behavior for Si-O bonding predominates over cation-OH bonding as a control on temperature-dependent ^{18}O fractionation in the hydrous Mg-silicates.

The fully calibrated brucite-water fractionation curve can also be used to develop mineral-brucite geothermometers for application in diverse geologic settings. For example, the calcite-brucite fractionation curve is a potentially useful geothermometer in metamorphosed carbonate rocks where brucite coexists with calcite. We have computed this fractionation curve using data for calcite from Friedman and O'Neil (1977), together with the experimental results for brucite-water described by equation (4) above (Fig. 6). The result shows that calcite is significantly enriched in ^{18}O relative to brucite and the temperature dependence is steep with the fractionation decreasing by 20‰ from 25-450°C. For example, Kretz (2001) reports a calcite-brucite ^{18}O fractionation of 19.7‰ from Grenville marbles in the Otter Lake area of western Quebec. This corresponds to a temperature of 100°C using the calcite-brucite fractionation curve in Fig. 6, consistent with brucite formation during retrograde metamorphism assuming that the observed fractionation represents the equilibrium condition.

Serpentine-brucite ^{18}O fractionation is another geothermometer of interest due to the common association of brucite with serpentized ultramafic rocks. The brucite-water fractionation curve (equation 4) can be combined with data for serpentine-water from experiments (Saccoccia et al, 2009) or natural samples (Wenner and Taylor, 1971) to compute

independent serpentine-brucite fractionation curves (Fig. 6). Zheng (1998) has also predicted serpentine-brucite fractionation based on application of the increment method (Fig. 6). The curve for serpentine-brucite based solely on experiments shows a steeper dependence on temperature and the curves based on the increment method and data from natural samples for serpentine are in generally good agreement. Wenner and Taylor (1974) report a serpentine (antigorite)-brucite fractionation of 4.9‰ from vein formations associated with altered ultramafic rocks in Vermont. Zheng (1998) indicated that this fractionation yields an isotopic temperature of 350°C using the increment method. A slightly lower temperature of 335°C is indicated by the serpentine-brucite fractionation calibrated by experiment. Zheng (1998) calculates a similar temperature of 370°C from serpentine-magnetite fractionation in these same samples, suggesting that the isotopic temperatures are representative of those associated with serpentine formation during retrograde metamorphism. More $\delta^{18}\text{O}$ measurements for brucite from these and other geologic settings are needed to further test the geothermometers in Fig. 6.

3.3. Portlandite-Water

Portlandite-water equilibrium ^{18}O fractionation factors are substantially more negative than those for brucite-water, decreasing from -11.1‰ at 125°C to -11.6‰ at 200°C, and then increasing to -6.6‰ at 425°C (Table 3). These experimental results can be described by the equation:

$$10^3 \ln \alpha_{\text{portlandite-water}} = 5.61 \times \frac{10^6}{T^2} - 26.29 \times \frac{10^3}{T} + 19.72 \quad (5)$$

where T is temperature in Kelvin. Equation (5) can be used to compute the equilibrium oxygen isotope fractionation factor between portlandite and pure water from 125° to 425°C (Fig. 4). Similar to brucite, portlandite incorporates less ^{18}O into its structure relative to coexisting water.

The temperature dependency shown is steeper than that of brucite, and indicates that portlandite incorporates progressively more ^{18}O into its structure relative to water as temperature increases above 200°C. A minimum in the fractionation factor for portlandite between 100 and 200°C is suggested by the data (Fig. 4), although experiments at temperatures below 125°C are needed to confirm this conclusion.

3.4 Comparison with Increment Method

The availability of experimentally derived equilibrium mineral-water oxygen isotope fractionation factors for brucite and portlandite represents an opportunity to evaluate the accuracy of the increment method deployed by Zheng (1998) to predict ^{18}O fractionation for hydroxide minerals. Given the structural similarity of brucite and portlandite, comparison of equilibrium brucite-portlandite fractionation provides a direct assessment of how well the increment method incorporates the relative effect of cation mass on ^{18}O fractionation in cation-OH bonds. In addition, comparing the ^{18}O fractionation against that of a known reference mineral such as quartz allows an assessment of how well the model predicts the absolute magnitude of the fractionation factors. If agreement exists, then the model may be applied with more confidence to other OH-bearing minerals, particularly at low temperature where experimental calibration is often difficult.

The results of this study indicate that at equilibrium brucite is enriched in ^{18}O relative to portlandite by approximately 8‰ at 125°C to 3‰ at 425°C (Fig. 7). The temperature dependent equilibrium fractionation between brucite and portlandite from 125 to 425°C can be described by the following equation:

$$10^3 \ln \alpha_{\text{brucite-portlandite}} = -1.22 \times \frac{10^6}{T^2} + 9.34 \times \frac{10^3}{T} - 8.53 \quad (6)$$

Equation (6) indicates that this mineral pair could be used as a geothermometer, although the rarity of portlandite and their very different solubilities (Walther, 1986; Seewald and Seyfried, 1991) makes brucite-portlandite an unlikely mineral assemblage in nature. This observed fractionation is consistent with stable isotope theory which predicts a decrease in the cation mass effect on isotopic substitution as temperature increases (Urey, 1947). The observed preference for ^{18}O in brucite relative to portlandite likely reflects a difference in vibrational energy on the molecular level within the two phases. As previously discussed, the degree to which one molecule prefers the heavier isotope compared to another (fractionation between two minerals) is controlled by the degree to which the substitution lowers the molecule's vibrational energy (Urey, 1947; see also review in Chacko et al, 2001). In general, bonds involving cations with a lower atomic mass will have a higher lattice vibration frequency. These bonds will therefore favor ^{18}O to stabilize the structure relative to bonds with heavier cations. In this way, we can qualitatively attribute the relative ^{18}O enrichment observed in this study ($\text{Ca}(\text{OH})_2 < \text{Mg}(\text{OH})_2$), to the significantly smaller mass of Mg compared to Ca within cation-OH bonds. Carbonate minerals with a larger cation mass also incorporate less ^{18}O into the mineral structure (O'Neil et al, 1969; Tarutani et al, 1969; Kim and O'Neil, 1997), consistent with the results of this study.

The increment method is in poor agreement with the experimental calibration of brucite-portlandite ^{18}O fractionation (Fig. 7). The predicted fractionation is slightly negative suggesting a preference for ^{18}O in portlandite relative to brucite, in contrast to what we observe by experiment. Moreover, the fractionation is quite small (-0.1 to -0.2‰) despite the large mass difference between Ca and Mg, and exhibits no significant dependence on temperature (Fig. 7). The sequence of ^{18}O enrichment predicted by Zheng (1998) extends to even heavier cations: $\text{Mg}(\text{OH})_2 < \text{Ca}(\text{OH})_2 < \text{Mn}(\text{OH})_2 < \text{Cu}(\text{OH})_2$. Thus, molecules with heavier divalent cations such

as Mn and Cu are predicted to incorporate even more ^{18}O into the hydroxide structure, which does not align with basic theory. Comparison with the experimental calibration presented here indicates that the increment method does not adequately parameterize the relative affinity for ^{18}O in Mg-OH and Ca-OH bonds within pure hydroxides.

As previously mentioned, Zheng (1998) used the Si-O bond as a reference to compute the ^{18}O index, which ranks the hydroxide minerals according to their affinity for ^{18}O relative to quartz. The ^{18}O index is then linked to the reduced partition function ratios of quartz to compute absolute fractionation factors. Comparison of quartz-brucite and quartz-portlandite equilibrium fractionation predicted from the increment model with the experimental calibration reveals good agreement between the approaches for brucite up to 350°C, but there is a discrepancy of up to 2‰ at 375-450°C (Fig. 8). In those cases, the increment model predicts fractionation factors for quartz-brucite that are too large, under-estimating the affinity for ^{18}O in the OH group relative to the Si-O bond at higher temperature. This, in turn, accounts for the model's tendency to predict a flatter minimum in the brucite-water equilibrium fractionation curve (Fig. 4), with brucite predicted to be too depleted in ^{18}O relative to the experimental calibration above 350°C. The comparison for quartz-portlandite shows poor agreement overall, and the magnitude of the discrepancy increases systematically with decreasing temperature (Fig. 8). In this case, the increment model predicts equilibrium fractionation factors that are too small, over-predicting the amount of ^{18}O that fractionates into the Ca-OH bond relative to the Si-O bond in quartz, and by extension, the Mg-OH bond in brucite.

Chacko et al (1996) compared quartz-mineral equilibrium ^{18}O fractionation factors for anhydrous silicates, oxides, and hydrous silicates calculated from the increment model and calibrated from experiment at 1000 K. The agreement is good for anhydrous silicates, suggesting

that the model accurately captures ^{18}O fractionation involving Si-O, Al-O, and Si-O-M $^{2+}$ bonds. Discrepancies were noted, however, for oxides (rutile and magnetite) and hydrous silicates (muscovite and phlogopite). For the oxides the predicted values were too small by approximately 0.5‰ for rutile and 1.0‰ for magnetite. Thus, with increasing cation mass (Si-O to Ti-O to Fe-O bonding) the model appears to incorporate excess ^{18}O into the oxide structure relative to quartz, similar to the results of our analysis above for hydroxide minerals. For the hydrous silicates the calculated values were too large by 0.6-0.7‰, suggesting that the model underestimates the affinity for ^{18}O in the hydroxyl group relative to aluminosilicate oxygen (Chacko et al, 1996), again consistent with our analysis above for brucite at higher temperature. These comparisons led Chacko et al. (2001) to conclude that the increment method does not adequately parameterize the effect of cation mass within oxides and the presence of hydroxyl groups within hydrous silicates on ^{18}O fractionation. These same effects appear to apply to the pure hydroxide minerals as well.

Based on the analysis above, the discrepancies between the increment method (Zheng, 1998) and our experimental results may reflect the choice of Si-O as a reference and/or how Mg-OH and Ca-OH bonds were parameterized in the model. The ^{18}O index is controlled by key variables that include bond strength and a separate term for the effect of cation mass on isotope substitution. There is also a coupling coefficient that depends on the cation bond type. For the hydroxides, assumptions are made regarding the treatment of OH groups to create a structural model for a crystal with which the above parameters are computed. In the selection of Si-O as a reference, it was argued by Zheng (1998) that cation-OH bonds in hydroxide minerals behave similarly to the Si-O bond in silicates from the standpoint of their ^{18}O fractionation behavior. This is true at lower temperatures (up to 250°C), but we have shown here that ^{18}O becomes

progressively enriched in Mg-OH and Ca-OH bonds relative to water as temperature increases above 250°C (Fig. 4). Over this same temperature interval, the Si-O bond (quartz-water fractionation) becomes progressively more depleted (Matsuhisa et al. 1979). In this way, the agreement noted here between the measured and predicted ^{18}O fractionation behavior for brucite from 15-350°C (Fig. 8) could be related to the fact that brucite was modeled as an Mg-O bond and the mass of Mg is more similar to the Si-O reference compared to Ca. At higher temperatures, however, modeling the Mg-OH bond in brucite with that approach could account for the discrepancies noted above given the different temperature dependent ^{18}O fractionation behavior of cation-OH vs Si-O bonds at those conditions. For quartz-portlandite fractionation, we attribute most of the discrepancy noted in Fig. (8) to the cation mass effect. This conclusion is supported by the fact that these discrepancies track very closely in both magnitude and direction to those noted for brucite-portlandite fractionation in Fig (7). The largest difference between the experiments and the predictions is approximately 8‰ at 125°C, whereas the closest agreement occurs at the highest temperature investigated (425°C), which is where stable isotope theory predicts that the mass effect on ^{18}O fractionation behavior should be minimized.

Given that brucite-water equilibrium fractionation is now well calibrated by experiments over a large temperature range, one possibility to explore might be to use the Mg-OH bond in brucite as the reference to compute the ^{18}O index for other hydroxides. In this context, our results could be used to better fit cation-specific indices in the increment method and thereby improve prediction of ^{18}O fractionation factors for hydroxides and hydroxyl-bearing aluminosilicate minerals. Our results document that cation mass within hydroxyl bonds has a significant effect on ^{18}O fractionation, especially at lower temperatures. It is at these conditions where the

increment method is potentially most useful as a tool to predict fractionation factors for minerals that are difficult to calibrate by experiment.

4. CONCLUSIONS

Oxygen isotope fractionation in the brucite-water and portlandite-water systems was determined by experiment from 125 to 425°C at 50 MPa. For the brucite-water system, the fractionation factor shows little variation from 200-300°C (-4.7‰) but increases to -3.5‰ at 425°C. These values are consistent with previous experimental results for brucite from 250 to 450°C (Saccocia et al. 1998) and smoothly connect with the low temperature experimental calibration of brucite-water fractionation from 15-120°C (Xu and Zheng, 1999). Taken together, the experimental calibrations from 15 to 450°C confirm that equilibrium ^{18}O brucite-water fractionation factors decrease with increasing temperature to 200°C, reach a broad minimum at ~250°C, and then increase with temperature to 450°C. This complex temperature dependency is unique when compared to hydroxyl-bearing Mg-silicates which have fractionation factors that decrease from 250-450°C, reflecting the relative influence of cation-OH and Si-O bonding on ^{18}O fractionation within these phases. The results of this study allow for the development of more reliable ^{18}O geothermometers involving brucite at moderate temperatures. Calcite-brucite is shown to be a suitable geothermometer applicable to metamorphosed carbonates where the two minerals occur together. Independent brucite-serpentine geothermometers can be determined using equation (4) and data for serpentine from experiments (Saccocia et al. 2009) and natural samples (Wenner and Taylor, 1971). These are broadly consistent with the geothermometer

predicted using the increment method (Zheng, 1998) and can be applied to brucite-serpentine pairs in altered ultramafic rocks.

Portlandite-water ^{18}O fractionation factors are more negative than those for brucite and vary from $-11.1 \pm 2.7\text{‰}$ at 125°C , to $-11.6 \pm 1.4\text{‰}$ at 200°C , to $-6.6 \pm 0.1\text{‰}$ at 425°C . This result indicates that the fractionation factor for portlandite increases from 200 – 425°C and appears to display a minimum between 100 and 200°C . This indicates that brucite has a greater affinity for ^{18}O relative to portlandite, with brucite-portlandite ^{18}O fractionation decreasing from 8‰ at 125°C to 3‰ at 425°C . We therefore document a significant temperature dependent effect of cation mass on ^{18}O fractionation for Mg-OH and Ca-OH bonds within hydroxide minerals. A comparison of quartz-mineral ^{18}O fractionation predicted by the increment method (Zheng, 1998) with those measured by experiment yields good agreement for brucite up to 350°C but poor agreement for portlandite with the discrepancy increasing systematically with decreasing temperature. Thus, we conclude that the increment method, as it is applied to pure hydroxide minerals, does not adequately model the effect of cation mass on ^{18}O fractionation which is particularly significant at lower temperature. Our experimental results could be used to fit cation-specific parameters within the increment method to better predict ^{18}O mineral-water fractionation for a wide variety of hydroxyl-bearing phases, especially at low temperatures where calibration by experiment is difficult.

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FIGURE CAPTIONS

Figure 1: SEM images of reactant and product phases from select isotope exchange experiments: Initial reagent grade amorphous brucite (A) and cryptocrystalline portlandite (B). Brucite crystals (C) and portlandite crystals (D) formed during isotope exchange with water at 425°C for 14 days. Brucite crystals (E) and portlandite crystals (F) formed during isotope exchange with water at 300°C for 22 days. Significant recrystallization of the initial solid charge is observed which facilitated the exchange of isotopes.

Figure 2: Measured brucite-water oxygen isotope fractionation as a function of time during exchange experiments. The uncertainty in the measured fractionation ($\pm 0.2\text{‰}$) is smaller than the symbol size. The initial fractionation (0 days) brackets the inferred equilibrium distribution of isotopes and the degree of exchange is dependent on both time and temperature with the percent exchange varying from 40% at 200°C to 94% at 425°C.

Figure 3: Measured portlandite-water oxygen isotope fractionation as a function of time during exchange experiments. The uncertainty in the measured fractionation ($\pm 0.2\text{‰}$) is smaller than the symbol size. The initial fractionation (0 days) brackets the inferred equilibrium distribution of isotopes and the degree of exchange is dependent on both time and temperature with the percent exchange varying from 54% at 125°C to 95% at 425°C.

Figure 4: Equilibrium oxygen isotope fractionation factors for brucite-water and portlandite-water as a function of temperature. The experimental points from this study represent the average and standard deviation of six determinations of the fractionation factor using equation (3). Where

no error bars are shown the reported uncertainty is less than the symbol size. All experimental data for brucite from 15 to 450°C (Saccocia et al, 1998; Xu and Zheng, 1999; this study) define a single smooth function (solid line) described by equation (4). This confirms the existence of a broad minimum in the fractionation curve at ~250°C. The fractionation factor for portlandite is significantly more negative than that for brucite, indicating that portlandite has a relative affinity for ^{16}O . The solid curve for portlandite represents a polynomial fit of the data described by equation (5). The empirical predictions (Zheng, 1998) depart from the experimental calibration at temperatures above 350°C for brucite and are in poor agreement with the experimental calibration for portlandite.

Figure 5: A comparison of mineral-water ^{18}O fractionation factors for brucite and hydrous Mg-silicates calibrated by laboratory experiments: (1, 2) Saccocia et al. (2009), (3) Cole and Ripley (1999), (4) Saccocia et al (1998); Xu and Zheng (1999); this study. The sequence shown for ^{18}O enrichment from brucite to talc reflects the relative influence of cation-OH and Si-O bonding on ^{18}O fractionation within these phases.

Figure 6: Mineral-brucite ^{18}O fractionation as a function of temperature. The calcite-brucite curve was derived using equation (4) from this study and calcite-water fractionation from Friedman and O'Neil (1977). Calcite-brucite ^{18}O fractionation reported from Grenville marbles (Kretz, 2001) yields an isotopic temperature of 100°C, consistent with brucite formation during retrograde metamorphism. For serpentine-brucite, equation (4) from this study was used together with experimental data for serpentine (Saccocia et al, 2009) for curve (2) and data from natural samples (Wenner and Taylor, 1971) for curve (3). The increment method (Zheng, 1998) was

used for curve (4). Serpentine (antigorite)-brucite fractionation from altered ultramafic rocks (Wenner and Taylor, 1974) suggest serpentinization temperatures of 335°C (curve 2) to 350°C (curves 3, 4).

Figure 7: Brucite-portlandite ^{18}O - ^{16}O fractionation as a function of temperature determined by experiment (this study) and predicted using the increment method (Zheng, 1998). The open square is a tentative data point based on the measured brucite-water fractionation at 120°C (Xu and Zheng, 1999) and the portlandite-water fractionation at 125°C from this study. The curve was computed from the polynomial fits (equations 4 and 5) and is valid from 125-425°C, which is the temperature range over which mineral-water fractionation has been calibrated for both minerals.

Figure 8: A comparison of quartz-brucite and quartz-portlandite ^{18}O fractionation calibrated by experiments and predicted using the increment method (Zheng, 1998). The solid line shows where the two methods are in agreement. For quartz-brucite, the two methods agree up to 350°C, but at higher temperatures the predicted fractionation factors are too large by 2‰. Poor agreement is noted for quartz-portlandite over the entire calibrated range with the discrepancy increasing systematically with decreasing temperature.

Table 1

Table 1: Oxygen isotope data for brucite-water exchange experiments

Initial Fluid Enriched in ¹⁸ O						Initial Fluid Depleted in ¹⁸ O					Initial Fluid Intermediate in ¹⁸ O					Calculated Brucite-Water Fractionation*							
brucite			water			brucite			water			brucite			water			10 ³ lnα		10 ³ lnα		10 ³ lnα	
Days	grams	δ ¹⁸ O	grams	δ ¹⁸ O	10 ³ lnα	grams	δ ¹⁸ O	grams	δ ¹⁸ O	10 ³ lnα	grams	δ ¹⁸ O	grams	δ ¹⁸ O	10 ³ lnα	enr-dep	% ex	enr-int	% ex	dep-int	% ex		
Temperature = 200°C																							
0		-2.9		52.3	-53.9		-2.9		-49.7	48.1		-2.9		-7.3	4.4								
134	0.202	22.7	1.488	50.2	-26.5	0.206	-23.7	1.426	-47.9	25.1	0.200	-7.9	1.507	-6.8	-1.1	1.5	49.4	-5.4	56.4	-9.4	40.0		
148	0.205	23.3	1.502	50.1	-25.8	0.215	-29.6	1.493	-47.3	17.5	0.200	-7.8	1.507	-6.8	-1.0	-4.3	56.6	-5.0	57.4	-5.4	55.5		
Temperature = 300°C																							
0		-2.9		52.3	-53.9		-2.9		-49.7	48.1		-2.9		-7.3	4.4								
14	0.200	28.4	1.487	49.7	-20.5	0.209	-35.8	1.498	-46.9	11.6	0.221	-8.4	1.480	-6.7	-1.7	-5.2	68.5	-4.6	67.8	-4.4	69.5		
22	0.203	30.7	1.471	49.4	-18.0	0.213	-36.7	1.486	-46.7	10.4	0.203	-8.9	1.495	-6.7	-2.2	-4.1	72.1	-4.7	73.0	-4.9	71.0		
Temperature = 375°C																							
0		-2.9		52.3	-53.9		-2.9		-49.7	48.1		-2.9		-7.3	4.4								
7	0.206	37.6	1.494	48.9	-10.8	0.205	-42.2	1.498	-46.4	4.4	0.196	-9.3	1.488	-6.7	-2.6	-3.3	85.1	-3.8	85.9	-4.0	83.9		
14	0.205	38.4	1.497	48.8	-10	0.203	-43.5	1.501	-46.3	2.9	0.200	-9.7	1.479	-6.7	-3.0	-3.6	87.4	-4.0	88.1	-4.2	86.4		
Temperature = 425°C																							
0		-2.9		52.3	-53.9		-2.9		-49.7	48.1		-2.9		-7.3	4.4								
8	0.195	38.1	1.359	48.7	-10.2	0.220	-36.1	1.245	-46.1	10.4	0.206	-9.7	1.221	-6.5	-3.2	0.9	79.8	-4.3	88.1	-6.7	68.7		
14	0.199	41.5	1.411	48.4	-6.7	0.192	-44.9	1.247	-45.7	0.9	0.209	-9.7	1.246	-6.5	-3.2	-2.9	92.7	-3.7	94.2	-4.0	90.7		

*Values computed by applying equation (3) to companion runs at each temperature condition. There are three companion runs and each was sampled on two occasions. Thus, six determinations of the fractionation factor are shown at each condition.

Table 2

Table 2: Oxygen isotope data for Portlandite-water exchange experiments

Initial Fluid Enriched in ¹⁸ O						Initial Fluid Depleted in ¹⁸ O					Initial Fluid Intermediate in ¹⁸ O					Calculated Portlandite-Water Fractionation*											
portlandite			water*			10 ³ lnα	portlandite		water		10 ³ lnα	portlandite		water		10 ³ lnα	10 ³ lnα		10 ³ lnα		enr-dep	% ex	enr-int	% ex	dep-int	% ex	
Days	grams	δ ¹⁸ O	grams	δ ¹⁸ O	grams		δ ¹⁸ O	grams	δ ¹⁸ O	grams		δ ¹⁸ O	grams	δ ¹⁸ O	grams		δ ¹⁸ O	enr-dep	% ex	enr-int							% ex
Temperature = 125°C																											
0		7.9		52.3	-43.1		7.9		-49.7	58.9		7.9		-7.3	15.2												
15	0.208	28.6	1.503	50.9	-21.5	0.216	-29.6	1.498	-47.1	18.2	0.211	-8.0	1.503	-6.3	-1.8	-7.7	61.1	-10.4	66.2	-15.9	54.4						
35	0.206	30.7	1.500	50.8	-19.3	0.215	-39.7	1.497	-46.4	7.0	0.193	-10.1	1.504	-6.0	-4.1	-11.0	74.2	-10.9	74.0	-10.7	74.6						
Temperature = 200°C																											
0		7.9		52.3	-43.1		7.9		-49.7	58.9		7.9		-7.3	15.2												
134	0.207	35.5	1.508	50.5	-14.3	0.208	-49.4	1.499	-45.9	-3.7	0.200	-15.5	1.498	-5.7	-9.9	-11.0	89.5	-12.0	92.3	-14.1	85.7						
148	0.202	38.1	1.502	50.3	-11.7	0.207	-53.1	1.499	-45.7	-7.8	0.208	-15.5	1.501	-5.7	-9.9	-10.4	96.2	-10.7	97.0	-11.2	95.1						
Temperature = 300°C																											
0		7.9		52.3	-43.1		7.9		-49.7	58.9		7.9		-7.3	15.2												
14	0.196	37.8	1.493	50.4	-12.1	0.194	-50.8	1.497	-46.0	-5.0	0.222	-11.5	1.483	-5.8	-5.7	-9.8	93.1	-8.3	89.2	-6.1	98.4						
22	0.198	38.4	1.51	50.3	-11.5	0.209	-50.2	1.485	-45.8	-4.6	0.202	-12.7	1.503	-5.9	-6.9	-9.1	93.4	-8.7	92.2	-8.1	94.9						
Temperature = 375°C																											
0		7.9		52.3	-43.1		7.9		-49.7	58.9		7.9		-7.3	15.2												
7	0.183	38.9	1.489	50.5	-11.1	0.205	-48.2	1.506	-46.0	-2.3	0.217	-11.0	1.461	-5.9	-5.2	-8.1	91.4	-7.5	89.8	-6.6	93.5						
14	0.203	40.1	1.497	50.2	-9.6	0.190	-50.0	1.499	-46.2	-4.1	0.195	-12.1	1.497	-6.0	-6.2	-7.7	94.4	-7.5	94.0	-7.3	95.0						
Temperature = 425°C																											
0		7.9		52.3	-43.1		7.9		-49.7	58.9		7.9		-7.3	15.2												
8	0.199	40.7	1.246	49.7	-8.7	0.204	-48.1	1.247	-45.3	-3.0	0.199	-11.1	1.239	-5.8	-5.4	-6.6	94.4	-6.6	94.4	-6.5	94.5						
14	0.200	40.6	1.238	49.7	-8.8	0.212	-47.6	1.246	-45.1	-2.6	0.199	-11.0	1.257	-5.8	-5.2	-6.5	94.0	-6.5	94.1	-6.6	94.0						

*Values computed by applying equation (3) to companion runs at each temperature condition. There are three companion runs and each was sampled on two occasions. Thus, six determinations of the fractionation factor are shown at each condition.

Table 3

Table 3: Oxygen isotope fractionation factors determined from exchange experiments*

T (°C)	Brucite-Water 1000ln α	Portlandite-Water 1000ln α	Brucite-Portlandite 1000ln α
125		-11.1 $\pm$ 2.7	
200	-4.7 $\pm$ 3.5	-11.6 $\pm$ 1.4	6.9 $\pm$ 3.8
300	-4.7 $\pm$ 0.4	-8.4 $\pm$ 1.3	3.7 $\pm$ 1.4
375	-3.8 $\pm$ 0.3	-7.5 $\pm$ 0.5	3.7 $\pm$ 0.6
425	-3.5 $\pm$ 2.5	-6.6 $\pm$ 0.1	3.1 $\pm$ 2.5

*Values for brucite and portlandite represent the average and standard deviation of six determinations of α_e using equation (3). For brucite-portlandite, the reported uncertainty is based on a propagation of error calculation using the standard deviations for each mineral-water pair.

FIGURE 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Figure 7

Figure 8