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## Oxygen isotope salt effects at high pressure and high temperature and the calibration of oxygen isotope geothermometers

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**Abstract**—The influence of NaCl, CaCl<sub>2</sub>, and dissolved minerals on the oxygen isotope fractionation in mineral-water systems at high pressure and high temperature was studied experimentally. The salt effects of NaCl (up to 37 molal) and 5-molal CaCl<sub>2</sub> on the oxygen isotope fractionation between quartz and water and between calcite and water were measured at 5 and 15 kbar and temperatures from 300 to 750°C. CaCl<sub>2</sub> has a larger influence than NaCl on the isotopic fractionation between quartz and water. Although NaCl systematically changes the isotopic fractionation between quartz and water, it has no influence on the isotopic fractionation between calcite and water. This difference in the apparent oxygen isotope salt effects of NaCl must relate to the use of different minerals as reference phases. The term *oxygen isotope salt effect* is expanded here to encompass the effects of dissolved minerals on the fractionations between minerals and aqueous fluids. The oxygen isotope salt effects of dissolved quartz, calcite, and phlogopite at 15 kbar and 750°C were measured in the three-phase systems quartz-calcite-water and phlogopite-calcite-water. Under these conditions, the oxygen isotope salt effects of the three dissolved minerals range from ~0.7 to 2.1‰. In both three-phase hydrothermal systems, the equilibrium fractionation factors between the pairs of minerals are the same as those obtained by anhydrous direct exchange between each pair of minerals, proving that the use of carbonate as exchange medium provides correct isotopic fractionations for a mineral pair.

When the oxygen isotope salt effects of two minerals are different, the use of water as an indirect exchange medium will give erroneous fractionations between the two minerals. The isotope salt effect of a dissolved mineral is also the main reason for the observation that the experimentally calibrated oxygen isotope fractionations between a mineral and water are systematically 1.5 to 2‰ more positive than the results of theoretical calculations. Dissolved minerals greatly affect the isotopic fractionation in mineral-water systems at high pressure and high temperature. If the presence of a solute changes the solubility of a mineral, the real oxygen isotope salt effect of the solute at high pressure and high temperature cannot be correctly derived by using the mineral as reference phase. Copyright © 2003 Elsevier Ltd

### 1. INTRODUCTION

Equilibrium oxygen isotope fractionation factors between two phases are the fundamental basis for the application of oxygen isotope thermometers and the discussion of any disequilibrium phenomena. The use of oxygen isotopes as a tool to model the interaction between rocks and aqueous fluids requires knowledge of the isotopic fractionation factors between minerals and aqueous fluids. Although theoretical calculations are useful in providing a basis for extrapolation of existing data beyond the range of experimental conditions, they are not yet accurate enough for a priori calculation of isotopic fractionation in mineral systems. Therefore, laboratory calibration has been the most important method for determining oxygen isotope fractionations between pairs of minerals and for providing a basis for constraining theoretical calculations.

The equilibrium fractionation between two silicates or two oxide minerals *A* and *B* cannot, in general, be obtained by direct exchange because of the difficulty of physical separation of very fine-grained products. Thus, the usual procedure has been to equilibrate each mineral separately with a third easily separated phase, referred to here as an exchange medium, such as

water, carbonate, carbon dioxide, or oxygen, and to obtain the fractionation between *A* and *B* as the difference of the fractionations of *A* and *B* relative to the common exchange medium.

Water and calcite have each been used as an exchange medium in the calibration of mineral-pair oxygen isotope thermometers. Theoretically, the fractionation factor between two minerals should not be affected by the selection of a different exchange medium. However, it has been observed that the fractionation factors between most common silicates and calcite obtained by direct anhydrous exchange are in significant disagreement with the fractionation factors obtained by combining silicate-water and calcite-water data (Chiba et al., 1989; Clayton et al., 1989). The discrepancies for fractionation factors obtained by hydrothermal exchange and by carbonate exchange for quartz-calcite, albite-calcite, anorthite-calcite, diopside-calcite, and magnetite-calcite pairs are shown in the appendix. They are typically in the range of 0.5 to 1.7‰ and are far beyond the claimed analytical uncertainty of ±0.15‰ for the determination of fractionation factors. For oxygen isotope thermometry at high temperature, a change of 100°C corresponds to just a few tenths of 1‰. Thus, the observed discrepancies in fractionations for different mineral pairs can correspond to errors in calculated temperatures of up to several hundred degrees.

There is a self-evident assumption in the use of a common

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exchange medium: every aspect of the exchange medium in different mineral-medium systems should be the same, so that the properties of the exchange medium will cancel. The fractionation between a mineral and aqueous fluid is a function of temperature (e.g., Urey, 1947), pressure (e.g., Polyakov and Kharlashina, 1994), and solute compositions (e.g., Feder and Taube, 1952; Horita et al., 1995; Driesner and Seward, 2000). Exchange experiments involving the same minerals have been conducted under both hydrothermal (mineral-water) and anhydrous (mineral-carbonate) conditions at the same pressure and temperature. This rules out the possibility that the discrepancies mentioned above are caused by temperature and pressure conditions and suggests that the discrepancies may be caused by the dependence of fractionations on solute compositions in the mineral-water systems.

In hydrothermal exchange experiments, pure water is usually used as the starting material. However, under high pressure and high temperature, minerals are somewhat soluble in water. Therefore, strictly speaking, in mineral-water systems under high pressure and high temperature, minerals exchange oxygen isotopes with different solutions rather than with a common pure water, and thus, the properties of exchange media may not cancel (Chacko, 1993). Knowledge of the influence of solute composition on the oxygen isotope fractionation between a mineral and aqueous fluid under high pressure and high temperature, therefore, is crucial in finding the reason(s) for the discrepancies in equilibrium fractionations between hydrothermal experiments and carbonate exchange experiments.

The influence of solute composition on oxygen isotope fractionation involving aqueous fluids, the so-called oxygen isotope salt effect, has been well determined below the critical temperature of water (e.g., Feder and Taube, 1952; Taube, 1954; Maiwald and Heinzinger, 1972; Sofer and Gat, 1972; Bopp et al., 1977; O'Neil and Truesdell, 1991; Horita et al., 1993a, 1993b, 1995; Shmulovich et al., 1999; Driesner et al., 2000; Driesner and Seward, 2000), with either CO<sub>2</sub> or water vapor as the reference phase. Kendall et al. (1983) and Zhang et al. (1989, 1994) investigated the isotope salt effect at higher temperature in mineral-salt-water systems using a mineral as reference phase. No oxygen isotope salt effect was found in these systems under the temperature and salinity conditions of their experiments. The influence of solute composition on isotopic fractionation at high pressure and high temperature remains unsolved.

Aqueous fluids with various amounts of salts, rather than pure water, are widespread on the surface and in the crust of the Earth. Very concentrated saline solutions with NaCl equivalent salt content up to 80 wt.% have been encountered in diverse geological settings (e.g., Roedder, 1971; Lowenstern, 1994; DeJong and Williams, 1995; Pasteris et al., 1995; Samson et al., 1995; Parry, 1998). Aranovich and Newton (1996) found that the water activity in NaCl solution at pressures of 10 kbar and greater is nearly equal to the square of its molar fraction. They invoked the effect of low water activity in concentrated salt solutions as a general mechanism in granulite-facies metamorphism. The study of oxygen isotope exchange between minerals and saline solution may have direct geological applications.

Above the critical point, CO<sub>2</sub> and water vapor are no longer suitable to be used as the reference phases in the study of isotope salt effects. A solid has to be used as the reference

phase. Quartz and calcite are two major rock-forming minerals, and they stably coexist with aqueous fluids in a wide range of pressure and temperature conditions. Furthermore, the oxygen isotope exchange between these two minerals and aqueous fluids is relatively fast at high temperature and high pressure. Therefore, quartz and calcite were chosen as the reference phases in this study to investigate the oxygen isotope salt effects at high pressure and high temperature.

NaCl and CaCl<sub>2</sub> are two of the most common salts encountered in natural fluids. In this study, the oxygen isotope salt effect of NaCl was experimentally investigated at 5 and 15 kbar at temperatures from 300 to 750°C, with quartz and calcite as reference phases. The oxygen isotope salt effect of CaCl<sub>2</sub> was investigated at 15 kbar and 600 and 750°C, with quartz as the reference phase. The oxygen isotope salt effects of dissolved quartz, calcite, and phlogopite were measured at 15 kbar and 750°C. The study of the effect of solute composition on isotopic fractionations in aqueous systems at high pressure and high temperature may not only provide answers to the discrepancy between hydrothermal exchange experiments and carbonate exchange experiments but also help us obtain a better understanding of natural fluid-rock interactions using oxygen isotopes.

## 2. CONVENTIONS

The influence of solute composition on isotope fractionations in hydrothermal systems is usually called the isotope salt effect. Thermodynamically, this means that the isotope ratios of aqueous solutions should be described in terms of activities rather than concentrations. Horita et al. (1993a) gave a rigorous definition of the oxygen isotope salt effect in a solution,  $\Gamma$ , as

$$\Gamma = \frac{R_{\text{solution}}^{\text{activity}}}{R_{\text{solution}}^{\text{composition}}} = \left( \frac{a_{\text{H}_2^{18}\text{O}}/a_{\text{H}_2^{16}\text{O}}}{X_{\text{H}_2^{18}\text{O}}/X_{\text{H}_2^{16}\text{O}}} \right)_{\text{solution}} = \left( \frac{\gamma_{\text{H}_2^{18}\text{O}}}{\gamma_{\text{H}_2^{16}\text{O}}} \right)_{\text{solution}}, \quad (1)$$

where  $R$ ,  $a$ ,  $X$ , and  $\gamma$  denote isotope ratio, activity, mole fraction, and activity coefficient, respectively. The subscript of  $R$  refers to the isotope ratio in a solution. The superscript refers to whether it is a ratio of isotopic activity or a ratio of isotopic composition. For practical determination of the isotope salt effect of a solution, a reference phase  $A$  has to be separately equilibrated with the solution and with pure water under the same pressure and temperature. Then, the isotope salt effect of the solution is (Horita et al., 1993a):

$$\Gamma = \frac{\alpha_{A\text{-solution}}}{\alpha_{A\text{-pure water}}}, \quad (2)$$

and  $1000\ln\Gamma = 1000\ln\alpha_{A\text{-solution}} - 1000\ln\alpha_{A\text{-pure water}} = \Delta_{A\text{-solution}} - \Delta_{A\text{-pure water}}$ .  $1000\ln\Gamma$  is measured in permil.

The real isotope salt effect of NaCl can be successfully determined with a mineral as a reference phase only if NaCl does not change the solubility of the mineral or if the dissolved mineral component does not affect the fractionation between the mineral and water. If NaCl affects the solubility of the mineral and the dissolved mineral itself has a measurable isotope salt effect, then the observed apparent isotope salt effect of NaCl in a mineral-NaCl-water system is the combination of the real isotope salt effect of NaCl and a net contribution of the difference in isotope salt effect of dissolved mineral in salt

solution and that in pure water. The net contribution is produced by the difference in the solubilities of the mineral in pure water and in NaCl solution under the same pressure and temperature.

For consideration of oxygen isotope salt effects of dissolved minerals at high pressure and high temperature, the following terms will be used in the rest of this paper:

- *Fractionation between mineral and water* for  $\Delta_{\text{mineral-water (mineral)}}$ : The word(s) in parentheses after water indicates that the water is saturated with respect to the dissolved mineral(s) at the temperature and pressure conditions of fractionation.  $\Delta_{\text{mineral-water (mineral)}}$  is the fractionation factor conventionally measured in a mineral-water system. It should be kept in mind that  $\Delta_{\text{mineral-water (mineral)}}$  is the fractionation between a mineral and an aqueous solution saturated with this mineral rather than between a mineral and pure, ion-free water.
- *Fractionation between mineral and ion-free water* for  $\Delta_{\text{mineral-ion-free water}}$ : Ion-free water is a hypothetical deionized water.  $\Delta_{\text{mineral-ion-free water}}$  is controlled only by temperature and pressure and is free from any isotope salt effect.
- *Isotope salt effect of dissolved mineral* for  $1000\ln\Gamma_{\text{dissolved mineral}} = \Delta_{\text{mineral-water (mineral)}} - \Delta_{\text{mineral-ion-free water}}$
- *Fractionation between a mineral and salt solution* for  $\Delta_{\text{mineral-salt solution (mineral)}}$ : The solutes in the salt solution consist of the salt and dissolved mineral. The salt solution is saturated with respect to the dissolved mineral under the pressure, temperature, and salt concentration of the experiment.
- *Apparent isotope salt effect of a salt* for  $1000\ln\Gamma_{\text{app salt}} = \Delta_{\text{mineral-salt solution (mineral)}} - \Delta_{\text{mineral-water (mineral)}}$ . All terms mentioned above are macroscopic properties.
- *Real isotope salt effect of a salt* for  $1000\ln\Gamma_{\text{real salt}}$ , which is the isotope effect caused solely by the interaction between water molecules and the salt at the molecular scale.
- *Indirect hydrothermal exchange* for the isotopic exchange between two minerals derived by separately exchanging each mineral with water and combining the two sets of exchange results.
- *Apparent fractionation between two minerals*,  $\Delta_{\text{app mineral A-mineral B}}$  for the fractionation between mineral A and mineral B by the indirect hydrothermal exchange method.
- Direct information about the isotope salt effects of dissolved minerals can be obtained by studying the isotope fractionations in a three-phase system consisting of two minerals, mineral A and mineral B, and water. In such a system, three fractionation factors can be measured:  $\Delta_{\text{mineral A-water (mineral A, mineral B)}}$ ,  $\Delta_{\text{mineral B-water (mineral A, mineral B)}}$ , and  $\Delta_{\text{mineral A-mineral B}}$ . Water in this system is saturated with dissolved mineral A and mineral B under the pressure and temperature conditions of exchange. Assuming that the presence of one mineral species in solution does not significantly affect the solubility of the second mineral species, the isotopic fractionation between mineral B and water in the system mineral A-mineral B-water can be expressed as

$$\Delta_{\text{mineral B-water (mineral A, mineral B)}} = \Delta_{\text{mineral B-ion-free water}} + 1000\ln\Gamma_{\text{dissolved mineral A}} + 1000\ln\Gamma_{\text{dissolved mineral B}} \quad (3)$$

The oxygen isotope salt effect of dissolved mineral A can be

obtained by comparing the fractionation factor  $\Delta_{\text{mineral B-water (mineral A, mineral B)}}$  and the fractionation factor between mineral B and water in a system of mineral B-water, which is

$$\Delta_{\text{mineral B-water (mineral B)}} = \Delta_{\text{mineral B-ion-free water}} + 1000\ln\Gamma_{\text{dissolved mineral B}} \quad (4)$$

Both  $\Delta_{\text{mineral B-water (mineral A, mineral B)}}$  and  $\Delta_{\text{mineral B-water (mineral B)}}$  are directly measurable. Therefore, the oxygen isotope salt effect of dissolved mineral A is

$$1000\ln\Gamma_{\text{dissolved mineral A}} = \Delta_{\text{mineral B-water (mineral A, mineral B)}} - \Delta_{\text{mineral B-water (mineral B)}} \quad (5)$$

The oxygen isotope salt effect of dissolved mineral B can be derived by the same procedure. The oxygen isotope salt effects of dissolved mineral A and dissolved mineral B measured in a three-phase hydrothermal system represent the real isotope salt effects of dissolved mineral A and mineral B only if the solubilities of mineral A and mineral B are the same in the mineral A-mineral B-water system as in the systems of mineral A-water and mineral B-water, respectively. However, even if the solubilities of minerals change in different assemblages, the isotope salt effects of minerals derived from the above method may still provide qualitative information about the signs and magnitudes of oxygen isotope salt effects of dissolved minerals.

The oxygen isotope fractionation between a mineral and a solution depends on the concentration and ionic species as well as their hydration (numbers) in the solution. Concentration and ionic species of dissolved minerals and the interaction between water molecules and ions are in turn a function of pressure and temperature. The solubilities, especially the types of ionic species and their hydration (numbers) of dissolved minerals at high pressure and high temperature, are not well known. Therefore, this experimental study will not attempt to discuss the isotope salt effect on a microscopic scale. The result of this study may help provide a basis to constrain further theoretical study on oxygen isotope salt effects at high pressure and high temperature.

### 3. EXPERIMENTAL METHODS

#### 3.1. Starting Materials

Starting quartz and calcite are natural samples. They were prepared by grinding in an agate mortar, followed by sedimentation in distilled water for 30 min. Scanning electron microscopy (SEM) studies showed that the size of mineral recovered from the suspended fraction that was used in this study ranges from 1 to 10  $\mu\text{m}$ . Syn-Ph1 and Syn-Ph2 (Table 1) are two synthesized phlogopite samples. Their X-ray diffraction patterns showed only the lines of phlogopite.

Oxygen isotope compositions of starting materials are shown in Table 1. Both  $\delta^{18}\text{O}$  and  $\delta^{17}\text{O}$  of starting quartz and phlogopite were measured by the conventional bromine pentafluoride method (Clayton and Mayeda, 1963). They follow the expected  $\delta^{17}\text{O} = 0.52 \times \delta^{18}\text{O}$  relation for normal terrestrial samples (Clayton et al., 1973) within analytical uncertainty ( $\pm 0.1\%$  for both  $\delta^{18}\text{O}$  and  $\delta^{17}\text{O}$ ). Because the two starting calcites, C1 and C4, are natural minerals, their starting  $\delta^{17}\text{O}$  values were assigned as  $0.52 \times \delta^{18}\text{O}$ . Oxygen was extracted from water and  $\text{CaCl}_2$  solution by reaction with bromine pentafluoride (O'Neil and Epstein, 1966). Waters of different isotopic compositions were used so that equilibrium could be approached from opposite directions. MEOW11 and  $\text{CaCl}_2$  solution have unusual oxygen isotope compositions in which their  $\delta^{17}\text{O}$  values are below the terrestrial fractionation line by  $> 9\%$ . With starting water whose isotopic com-

Table 1. Oxygen isotopic composition of starting materials.

Symbol	Description	$\delta^{18}\text{O}_{\text{SMOW}}^{\text{a}}$ (‰)	SD (1 $\sigma$ ) of $\delta^{18}\text{O}$ (‰)	$\delta^{17}\text{O}_{\text{SMOW}}$ (‰)	SD (1 $\sigma$ ) of $\delta^{17}\text{O}$ (‰)
<i>Minerals</i>					
Q	Natural quartz	12.17 (11)	0.07	6.32 (4)	0.10
Q2	Natural quartz	12.40 (4)	0.08	6.48 (3)	0.09
C1	Natural calcite	13.67 (4)	0.05	7.11 <sup>b</sup>	
C4	Natural calcite	14.10 (2)	0.05	7.34 <sup>b</sup>	
H-Cc	Natural calcite	17.52 (2)	0.07	9.11 <sup>b</sup>	
Syn-Ph1	Synthetic phlogopite	-8.97 (3)	0.07	-4.70 (2)	0.08
Syn-Ph2	Synthetic phlogopite	9.56 (4)	0.08	4.94 (2)	0.02
<i>Water</i>					
L-H <sub>2</sub> O		-7.67 (6)	0.12		
H-H <sub>2</sub> O		28.23 (4)	0.05		
MEO11		11.24 (4)	0.05	-3.97 (4)	0.08
CaCl <sub>2</sub> -solution		11.02 (2)	0.01	-3.80 (2)	0.08

All silicate and water analyses were done by BrF<sub>5</sub> reaction (Clayton and Mayeda, 1963; O'Neil and Epstein, 1966).

<sup>a</sup> Number of measurements is in parentheses. SMOW = standard mean ocean water.

<sup>b</sup>  $\delta^{17}\text{O} = 0.52 \times \delta^{18}\text{O}$ .

position is below the terrestrial fractionation line, the three-isotope exchange method (Matsuhisa et al., 1979) could be used, and the equilibrium fractionation factor could be derived from a single experiment. All water analyses were done by fluorination, so that no uncertainties due to CO<sub>2</sub>-H<sub>2</sub>O fractionations were introduced.

### 3.2. Isotopic Exchange Reaction

All oxygen isotope exchange experiments were carried out in a 1.91-cm piston-cylinder apparatus with a graphite heater and a NaCl pressure medium. Temperatures were controlled and measured with W-3% Re vs. W-25% Re thermocouples for experiments from 400 to 750°C. Chromel-alumel thermocouples were used for experiments at 300°C. The accuracy of temperature measurement is estimated to be better than  $\pm 5^\circ\text{C}$  (Aranovich and Newton, 1996). Pressures were measured with a Heise bourdon tube gauge. The accuracy of pressure is  $\sim \pm 200$  bar (Aranovich and Newton, 1996).

For exchange experiments between mineral and NaCl solution, NaCl was baked at 350°C for 1 h before loading into a 2.4-mm-diameter platinum capsule. After solids were loaded, the capsule was dried at 120°C for 2 h and then cooled to room temperature in a desiccator to minimize the absorption of moisture. Then water was added and the capsule was sealed by arc welding. For exchange experiments in the quartz-NaCl-water system, 10 to 12 mg of quartz and 6 to 7.2 mg of water with various amounts of NaCl from  $\sim 2.6$  to  $\sim 12.8$  mg were used. For exchange experiments in the calcite-NaCl-water system, each charge consisted of 11 to 13.3 mg of calcite, 6 to 7.2 mg of water, and various amounts of NaCl from  $\sim 2.6$  to  $\sim 12.8$  mg. In both quartz-NaCl-water and calcite-NaCl-water systems, NaCl concentrations range from 6.2 to 37.0 molal at 750°C, to 23.8 molal at 600°C, and to 13.9 molal at 500 and 400°C. At each temperature and pressure condition, the amount of NaCl varied from zero to around saturation, as determined by Aranovich and Newton (1996). In every experiment, the atomic ratio of oxygen in mineral and water is  $\sim 1:1$ . For the exchange between quartz and CaCl<sub>2</sub> solution,  $\sim 12$  mg of quartz and 5-molal CaCl<sub>2</sub> solution that contains the same amount of oxygen as quartz were loaded into a capsule.

For the exchange between phlogopite and water,  $\sim 13.9$  mg of phlogopite and 7.2 mg of water were used. For exchange in silicate-calcite-water systems, the silicate and calcite with 1:1 oxygen atomic ratio were first mixed under reagent-grade acetone in a small agate mortar three times to dryness. Then, the mixture was baked at 300°C for 3 h. No isotopic composition changes of the minerals in the mixture during the baking process were observed. For anhydrous direct exchange between silicate and calcite, a 25- to 30-mg charge was used. For hydrothermal exchange among silicate, calcite and water, the charge consisted of  $\sim 25$  mg of solid and 7.5 to 8.2 mg of water. The oxygen atomic ratios among silicate, calcite and water varied from 1:1:1.05 to 1:1:1.16 for hydrothermal exchanges.

### 3.3. Isotopic Analysis

After quenching, water was quantitatively recovered by puncturing the capsule in a vacuum system, monitored by comparing the weight of water loaded in the capsule and the amount of O<sub>2</sub> extracted from the water. Oxygen was extracted from water by reaction with bromine pentafluoride (O'Neil and Epstein, 1966). After removal of water, the capsule was cut open to recover the mineral. For an experiment between mineral and saline solution, salt was removed by washing the sample with distilled water. The mineral was then dried at 100°C for 1 h. Oxygen was extracted from quartz and phlogopite by reaction with bromine pentafluoride (Clayton and Mayeda, 1963). Both  $\delta^{18}\text{O}$  and  $\delta^{17}\text{O}$  were measured using O<sub>2</sub> as the sample gas. The oxygen isotope composition of calcite was determined by analyzing CO<sub>2</sub> liberated from calcite by reacting with 100% phosphoric acid for 1 d at 25°C (McCrea, 1950). Only  $\delta^{18}\text{O}$  was measured for calcite, with CO<sub>2</sub> as the sample gas.

The analytical procedure for products of anhydrous silicate-calcite exchange experiments was developed by Clayton et al. (1989) and Chiba et al. (1989). After cutting open the capsules, experimental products were recovered and crushed and ground. Then, a small portion was reacted with 100% phosphoric acid for 1 d at 25°C in the standard procedure for isotopic analysis of calcite. Calcite was removed from second portion by ultrasonically agitating it for 5 min in 2 N acetic acid solution and then letting it react with the acid solution for 1 h at room temperature. The solid residue was recovered by washing repeatedly with distilled water and then dried. The average recoveries of quartz and phlogopite were  $> 98\%$ . Oxygen isotope compositions of silicates were measured by the bromine pentafluoride method (Clayton and Mayeda, 1963). For experiments in silicate-calcite-water systems, after water was extracted, the analytical procedure for solids was similar to that of the experimental product of anhydrous direct exchanges between silicate and calcite described above.  $\delta^{17}\text{O}$  of calcite was obtained by fluorination of the CO<sub>2</sub> sample to convert it to O<sub>2</sub>. Controlled experiments of fluorination of CO<sub>2</sub> with both  $\delta^{18}\text{O}$  and  $\delta^{17}\text{O}$  values known showed that the  $\Delta^{17}\text{O}$  ( $\delta^{17}\text{O} - 0.52 \times \delta^{18}\text{O}$ ) value of CO<sub>2</sub> remains constant during fluorination. Therefore, the  $\delta^{17}\text{O}$  value of the CO<sub>2</sub> sample was obtained by  $\delta^{17}\text{O}_{\text{CO}_2} = 0.52 \times \delta^{18}\text{O}_{\text{CO}_2} + \Delta^{17}\text{O}_{\text{CO}_2}$ , where O<sub>2</sub> refers to the oxygen gas produced by fluorination of the CO<sub>2</sub> sample and  $\Delta^{17}\text{O}_{\text{O}_2} = \delta^{17}\text{O}_{\text{O}_2} - 0.52 \times \delta^{18}\text{O}_{\text{O}_2}$ .

The achievement of isotopic equilibrium is proved by the convergence of fractionations of run products approached from opposite directions or by the fact that the isotopic compositions of run products approached from opposite directions and lie on a secondary fractionation line in a three-isotope diagram. For experiments in which only partial exchange had been achieved, the method of Northrop and Clayton (1966) was used for runs with only  $\delta^{18}\text{O}$  values, and the three-isotope method of Matsuhisa et al. (1979) was used for runs with both  $\delta^{18}\text{O}$  and  $\delta^{17}\text{O}$  measurements.

Table 2. Oxygen isotopic fractionation between quartz and water at 15 kbar.

Run no.	<i>T</i> (°C)	<i>t</i> (h)	Water	<sup>18</sup> O <sub>MB</sub> <sup>a</sup> (‰)	<sup>17</sup> O <sub>MB</sub> <sup>a</sup> (‰)	<sup>18</sup> Δ <sub>f</sub> <sup>b</sup> (‰)	<sup>17</sup> Δ <sub>f</sub> <sup>b</sup> (‰)	Exchange <sup>c</sup> (%)	<sup>18</sup> Δ <sub>e</sub> <sup>c</sup> (‰)
QW1	750	72	L-H <sub>2</sub> O	-0.18		1.25		99	
QW2	750	72	H-H <sub>2</sub> O	0.15		0.93		99	1.10
QW11	750	72	MEOW11	0.04	0.18	1.20	0.95	98	1.20
QW36	750	144	MEOW11	-0.09	0.10	1.13	0.38	100	1.13
								Average	1.14
QW20	600	96	MEOW11	0.04	0.10	1.63	1.28	97	1.70
QW21	600	115	MEOW11	-0.13	-0.05	1.84	2.19	87	1.94
QW28	600	124	MEOW11	-0.09	0.16	1.82	1.66	93	1.87
								Average	1.84
QW26	500	258	MEOW11	0.06	0.11	2.47	2.94	83	2.78
QW39	500	312	MEOW11	-0.15	0.05	2.55	2.74	85	2.80
QW50	500	456	MEOW11	-0.07	0.07	2.49	2.34	89	2.61
								Average	2.73
QW14	400	541	MEOW11	-0.06	0.24	3.51	3.43	84	4.03
QW31	400	480	MEOW11	0.13	0.28	3.42	4.11	77	4.17
								Average	4.10

<sup>a</sup> Material balance,  $^{18}\text{O}_{\text{MB}} = \delta^{18}\text{O}_{\text{mean products}} - \delta^{18}\text{O}_{\text{mean reactants}}$ ,  $^{17}\text{O}_{\text{MB}} = \delta^{17}\text{O}_{\text{mean products}} - \delta^{17}\text{O}_{\text{mean reactants}}$ . Values should be  $0 \pm 0.2\text{‰}$ .

<sup>b</sup> Measured fractionation for the run products.  $\Delta = 1000\ln\alpha_{\text{mineral-water}}$ .

<sup>c</sup> Exchange extent and equilibrium fractionation factors are calculated on the basis of the method of Northrop and Clayton (1966) and the method of Matsuhisa et al. (1979).

X-ray studies showed that there was no change in mineral structure between starting mineral and run product for all experiments. SEM images revealed that the products of all hydrothermal exchange experiments had gone through a considerable dissolution-recrystallization process, and the amount of quench product was negligible.

## 4. EXPERIMENTAL RESULTS

### 4.1. Quartz-NaCl-CaCl<sub>2</sub>-Water System

Isotopic fractionations in the system quartz-NaCl-water were investigated at 15 kbar from 400 to 750°C and at 5 kbar at 600 and 750°C. To derive the apparent oxygen isotope salt effect of NaCl with quartz as the reference phase, the equilibrium fractionation factor for quartz-water under identical temperature and pressure conditions must be well determined. There are numerous published calibrations of quartz-water fractionations based on different methods. Sharp and Kirschner (1994) observed that different results may differ by > 1‰. Equilibrium fractionation factors for quartz-water were experimentally recalibrated in this study to provide a self-consistent basis for the derivation of apparent oxygen isotope salt effects of NaCl.

#### 4.1.1. Quartz-Water

Exchange between quartz and water was conducted at 15 kbar from 400 to 750°C. The experimental conditions and results are shown in Table 2, and the fractionations as a function of temperature are shown in Figure 1. For all runs except QW31 at 400°C, the extent of exchange was > 80%. At each temperature, at least two independent measurements of equilibrium fractionation factor were made. Within analytical uncertainty, which is  $\pm 0.15\text{‰}$  for 100% exchange and  $\pm 0.18\text{‰}$  for 80% exchange, the independent measurements at the same temperature gave identical results. The results of the present study, shown in Figure 1, may be approximated by a straight line. The equation of the least squares line is

$$1000\ln\alpha_{\text{quartz-water (quartz)}} = 2.35 \times (10^6/T^2) - 1.16, \quad (6)$$

where *T* is the temperature (K).

Quartz-water fractionations measured in this study are larger than those obtained by Clayton et al. (1972) by 0.45 to 0.65‰ from 400 to 750°C. The current experiments were carried out at 15 kbar, whereas those of Clayton et al. (1972) were conducted at 1 kbar. Besides the systematic difference in temperature measurements between this study and that of Clayton et al. (1972), as was discussed by Matsuhisa et al. (1979), the pressure-induced change of the solubility of quartz and its subsequent influence on the quartz-water fractionation, which will be discussed later, may contribute to the 0.45 to 0.65‰ difference.

Despite use of the same experimental apparatus and the same experimental conditions, the quartz-water fractionations obtained by this study are larger than those obtained by Matsuhisa et al. (1979) by 0.12 to 0.37‰ from 400 to 750°C. The reason for this discrepancy remains unsolved.

#### 4.1.2. Quartz-NaCl Solution at 15 kbar

Results of oxygen isotope exchange between quartz and NaCl solution at 15 kbar are shown in Table 3. At 750°C, all except one run reached equilibrium. The extent of exchange at 600°C was > 87%. Extents of exchange at 500°C were > 80% and at 400°C were > 60%. The concentration of NaCl does not have much effect on the exchange rate.

The variation of equilibrium fractionation factors with NaCl concentration at each temperature is shown in Figure 2. At 750°C, the addition of NaCl decreases the fractionation between quartz and fluid by as much as 0.85‰. The direction of the apparent NaCl oxygen isotope salt effect at 600°C is the same as at 750°C, but its magnitude is smaller ( $\leq 0.28\text{‰}$ ).

The presence of excess solid NaCl does not affect the fractionation between quartz and fluid. The solubility of NaCl at 15kbar and 600°C is  $\sim 24$  molal. The amount of NaCl of run

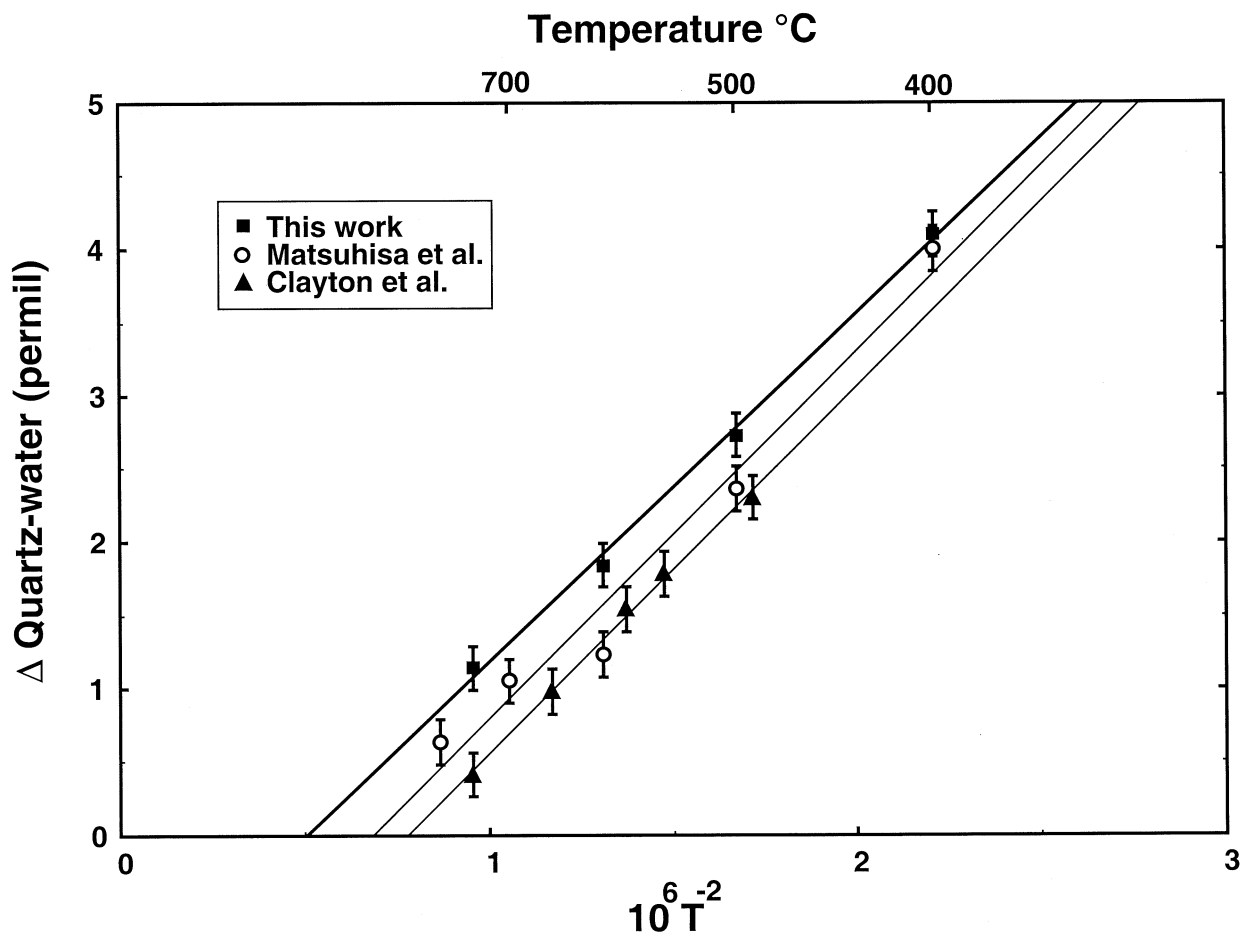


Fig. 1. Oxygen isotopic fractionation between quartz and water. Heavy line is a linear least squares fit to the experimental results. The experimental calibrations of Clayton et al. (1972) and Matsuhisa et al. (1979) are shown for comparison.

QS30 is equivalent to 37 molal, which is above saturation. The fractionation between quartz and this solution is 1.57‰, which is identical to the fractionation between quartz and 23.8-molal NaCl, as in runs QS23 and QS38, within analytical uncertainty.

At 500°C, the fractionation factor between quartz and water is identical to that between quartz and NaCl solution within analytical uncertainty of  $\pm 0.15\%$ , showing that the apparent oxygen isotope salt effect of NaCl at 500°C is negligible. In contrast to the apparent oxygen isotope salt effect of NaCl above 500°C, NaCl increases the fractionation between quartz and fluid at 400°C. The extent of exchange between quartz and NaCl solution is 61 to 76% at 400°C. The analytical uncertainties of the determination of equilibrium fractionation factors are  $\pm 0.25\%$  for an experiment with 61% exchange and  $\pm 0.20\%$  for a run with 76% exchange. Despite the relatively larger analytical uncertainty, the trend of positive apparent oxygen isotope salt effect of NaCl at 400°C is still obvious.

#### 4.1.3. Quartz-NaCl Solution at 5 kbar

Measurements of fractionations between quartz and 13.9-molal NaCl solution at 5 kbar are shown in Table 4. The exchange rate decreases with decreasing pressure (Matthews et al., 1983a). In an attempt to get a high extent of exchange to

derive reliable equilibrium fractionation factors, experiments were conducted only at 750 and 600°C. The extent of exchange was  $> 80\%$ . The fractionations at 5 kbar are  $\sim 0.4\%$  lower than those at 15 kbar at the corresponding temperature and salinity, as shown in Figure 2.

#### 4.1.4. Quartz-CaCl<sub>2</sub>-Water at 15 kbar

Experiments were conducted at 600 and 750°C. Quartz Q and a 5-molal CaCl<sub>2</sub> solution were used as starting materials. The results are shown in Table 5. At 15 kbar, with quartz as the reference phase, the apparent oxygen isotope salt effect of 5-molal CaCl<sub>2</sub> solution is 0.61‰ at 750°C and 0.68‰ at 600°C, compared to 0.22‰ and 0.15‰ for 6.2-molal NaCl at these temperatures.

## 4.2. Calcite-NaCl-Water System

### 4.2.1. Calcite-Water

Equilibrium fractionation factors between calcite and water were measured to provide a self-consistent basis for the derivation of apparent oxygen isotope salt effects of NaCl at high pressure and high temperature, with calcite as the reference

Table 3. Oxygen isotopic fractionation between quartz and NaCl solution at 15 kbar.

Run no.	<i>T</i> (°C)	<i>t</i> (h)	Water	NaCl molality (mol/kg H <sub>2</sub> O)	<sup>18</sup> O <sub>MB</sub> <sup>a</sup> (‰)	<sup>17</sup> O <sub>MB</sub> <sup>a</sup> (‰)	<sup>18</sup> Δ <sub>f</sub> <sup>b</sup> (‰)	<sup>17</sup> δ <sub>f</sub> <sup>b</sup> (‰)	Exchange <sup>c</sup> (%)	<sup>18</sup> Δ <sub>e</sub> <sup>c</sup> (‰)
QS24	750	116	MEOW11	6.2	0.00	0.22	0.97	0.35	100	0.97
QS33	750	122	MEOW11	6.2	0.00	0.08	0.87	0.06	100	0.87
									Average	0.92
QS3	750	72	L-H <sub>2</sub> O	13.9	0.13		0.68			
QS4	750	72	H-H <sub>2</sub> O	13.9	-0.18		1.22			0.95
QS5	750	72	MEOW11	13.9	-0.25	-0.33	0.73	0.02	100	0.73
QS15	750	144	MEOW11	13.9	0.06	-0.27	0.74	0.17	100	0.74
									Average	0.81
QS22	750	96	MEOW11	23.8	0.03	0.10	0.77	0.24	100	0.77
QS34	750	121	MEOW11	23.8	-0.22	-0.03	0.60	0.29	100	0.60
									Average	0.68
QS6	750	72	MEOW11	37.0	-0.20	-0.02	0.33	0.39	98	0.33
QS35	750	121	MEOW11	37.0	-0.29	0.03	0.24	0.08	100	0.24
									Average	0.29
QS37	600	119	MEOW11	6.2	0.08	0.27	1.57	1.74	91	1.66
QS42	600	93	MEOW11	6.2	0.04	0.15	1.67	1.97	88	1.72
									Average	1.69
QS8	600	70	MEOW11	13.9	-0.32	-0.02	1.70	1.78	96	1.72
QS19	600	93	MEOW11	13.9	0.01	0.00	1.48	2.09	87	1.57
									Average	1.64
QS23	600	86	MEOW11	23.8	0.01	0.19	1.53	1.64	92	1.57
QS38	600	119	MEOW11	23.8	-0.06	0.20	1.47	2.12	88	1.54
									Average	1.56
QS30	600	121	MEOW11	24 <sup>d</sup>	0.01	0.14	1.53	2.11	87	1.57
QS25	500	329	MEOW11	6.2	-0.13	0.08	2.51	2.60	87	2.74
QS44	500	328	MEOW11	6.2	0.10	0.15	2.40	2.74	84	2.64
									Average	2.69
QS41	500	310	MEOW11	13.9	-0.07	0.15	2.19	3.29	79	2.60
QS45	500	330	MEOW11	13.9	0.00	0.06	2.36	2.70	85	2.62
									Average	2.61
QS46	400	475	MEOW11	6.2	0.01	-0.02	3.26	4.87	67	4.25
QS47	400	496	MEOW11	6.2	0.03	0.02	3.38	4.10	76	4.16
									Average	4.21
QS48	400	472	MEOW11	12.2	0.16	0.04	3.23	4.80	70	4.35
QS10	400	235	MEOW11	13.9	-0.01	0.05	3.42	5.01	61	4.60

Notes a to c are the same as in Table 2.

<sup>d</sup> NaCl in this experiment is above saturation, which is ~ 24 molal. The amount of NaCl in QS30 is equivalent to 37 molal.

phase. Exchange experiments were conducted at five temperatures from 300 to 750°C at 15 kbar. The results of exchange experiments are shown in Table 6 and Figure 3. Exchange experiments at 500, 600, and 750°C reached equilibrium, as shown by the fact that <sup>18</sup>Δ<sub>final</sub> values of runs approaching from opposite directions converge or overlap within analytical uncertainty. Experiments at 400 and 300°C have exchange extents > 90%. Least squares regression of the present results yields the equation of a straight line:

$$1000\ln\alpha_{\text{calcite-water (calcite)}} = 2.01 \times (10^6/T^2) - 1.77, \quad (7)$$

where *T* is the temperature (K).

As is shown in Figure 3, the slope of the regression line of this study is smaller than that of O'Neil et al. (1969), and these two lines cross at ~400°C. The difference in the calcite-water fractionations obtained by this study and by O'Neil et al. (1969) varies from -0.30 to +0.28‰, with temperature ranging from 300 to 750°C.

#### 4.2.2. Calcite-NaCl-Water at 15 kbar

Isotopic fractionation between calcite and NaCl solution was investigated at 15 kbar from 300 to 750°C. Experi-

mental results are shown in Table 7. Except for the exchange between calcite and 13.9-molal NaCl solution at 600°C, all runs at 500°C and above reached equilibration, proved by the convergence of <sup>18</sup>Δ<sub>final</sub> values of runs from opposite directions. All runs at 300 and 400°C have exchange extents > 85%.

The fractionation factors between calcite and water and between calcite and NaCl solution are shown in Figure 4 at different temperatures as a function of NaCl concentration. Except for the decrease of 0.2‰ in 13.9-molal NaCl solution at 500 and 600°C, the addition of NaCl does not affect the fractionation between calcite and water within analytical uncertainty at all temperatures investigated in this study.

### 4.3. Quartz-Calcite-Water System

#### 4.3.1. Quartz-Calcite by Anhydrous Direct Exchange

Anhydrous direct exchange between quartz and calcite at 15 kbar and 750°C was also conducted in the present study, and the results are shown in Table 8. An equilibrium fractionation factor of 0.39‰ was measured for direct exchange between quartz and calcite at 15 kbar and 750°C. The quartz-calcite

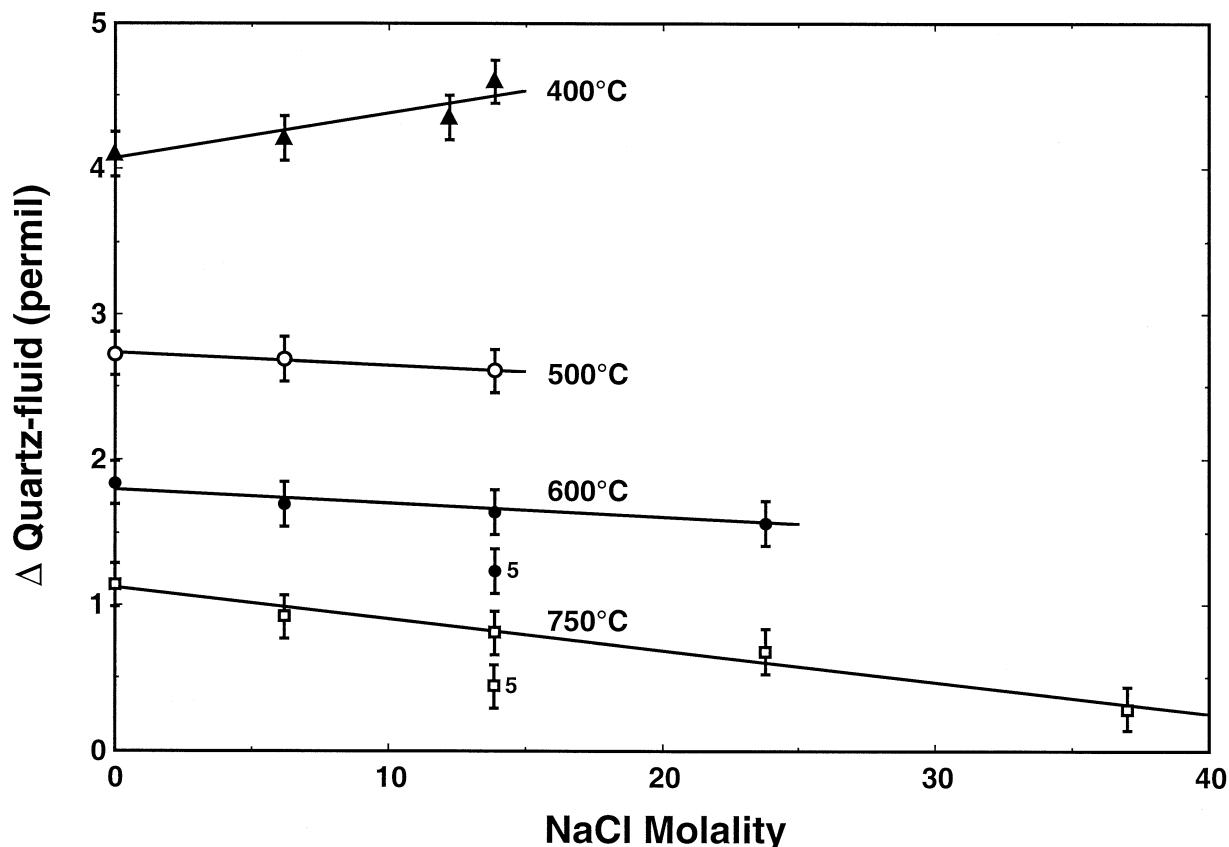


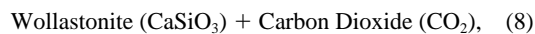
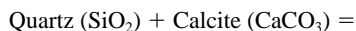
Fig. 2. Isotopic fractionation between quartz and saline solution as a function of the NaCl concentration at different temperatures and pressures. The symbols labeled with the number 5 are results of experiments carried out at 5 kbar. All others are results of experiments conducted at 15 kbar.

fractionation equation given by the direct exchange experiments of Clayton et al. (1989) yields a quartz-calcite fractionation of 0.36‰ at 750°C, which is identical to the present result.

#### 4.3.2. Quartz-Calcite-Water Fractionation in Three-Phase Hydrothermal System

Isotopic exchange experiments among quartz, calcite, and water in the system of quartz-calcite-water were conducted at 15 kbar and 750°C to investigate the oxygen isotope salt effects of dissolved quartz and dissolved calcite and their influence on the isotopic fractionation between quartz and calcite. The isotopic compositions of experimental products are shown in

Table 9. The following mineralogical reaction occurred to a small extent in the experiments:



shown by the detection of carbon dioxide in the fluid phase and a very weak line of wollastonite in the X-ray pattern of solid products. As shown in Table 9, the fractionation between carbon dioxide and water,  $^{18}\Delta_{\text{CO}_2\text{-H}_2\text{O}}$ , is  $40.54 \pm 0.02\%$ , which is the result of retrograde exchange between carbon dioxide and water at a temperature near 25°C (Bottinga, 1968; Brenninkmeijer et al., 1983) after quenching.

Table 4. Oxygen isotopic fractionation between quartz and 13.9-molal NaCl solutions at 5 kbar.

Run no.	$T$ (°C)	$t$ (h)	$^{18}\text{O}_{\text{MB}}^{\text{a}}$ (‰)	$^{17}\text{O}_{\text{MB}}^{\text{a}}$ (‰)	$^{18}\Delta_{\text{f}}^{\text{b}}$ (‰)	$^{17}\Delta_{\text{f}}^{\text{b}}$ (‰)	Exchange <sup>c</sup> (%)	$^{18}\Delta_{\text{c}}^{\text{c}}$ (‰)
1	750	89	0.24	0.11	0.50	0.44	98	0.49
4	750	90	0.23	0.19	0.40	0.24	100	0.40
							Average	0.45
2	600	164	0.25	0.13	1.30	2.24	84	1.36
3	600	100	0.11	0.09	1.10	2.30	82	1.12
							Average	1.24

Notes a to c are the same as in Table 2.



Table 5. Oxygen isotopic fractionation between quartz and 5-molal CaCl<sub>2</sub><sup>a</sup> solution at 15 kbar.

Run no.	<i>T</i> (°C)	<i>t</i> (h)	<sup>18</sup> O <sub>MB</sub> <sup>b</sup> (‰)	<sup>17</sup> O <sub>MB</sub> <sup>b</sup> (‰)	<sup>18</sup> Δ <sub>f</sub> <sup>c</sup> (‰)	<sup>17</sup> Δ <sub>f</sub> <sup>c</sup> (‰)	Exchange <sup>d</sup> (%)	<sup>18</sup> Δ <sub>e</sub> <sup>d</sup> (‰)
1	750	65	0.06	0.00	0.56	0.55	98	0.54
2	750	94	-0.01	0.05	0.52	0.32	100	0.52
							Average	0.53
3	600	144	0.05	0.13	1.18	1.54	90	1.18
4	600	144	0.07	0.08	1.13	1.53	90	1.13
							Average	1.16

<sup>a</sup> Initial: δ<sup>18</sup>O<sub>quartz</sub> = 12.17‰, δ<sup>17</sup>O<sub>quartz</sub> = 6.33‰; δ<sup>18</sup>O<sub>CaCl<sub>2</sub>-solution</sub> = 11.02‰; δ<sup>17</sup>O<sub>CaCl<sub>2</sub>-solution</sub> = -3.80‰.

Notes b to d are the same as notes a to c in Table 2.

The isotopic compositions of quartz, calcite, and water at 750°C are needed to obtain the equilibrium fractionation factors among them. The amount of carbon dioxide was precisely measured with a micromanometer. There was 6.0 μmol carbon dioxide in the product of run QCW1 and 9.0 μmol in run QCW2. The amount of water was also well determined by weighing and by monitoring the oxygen yield of the water fluorination. Combining the carbon dioxide-calcite fractionation (Chacko et al., 1991) and the water-calcite fractionation, a fractionation of 4.1‰ can be derived for the fractionation between carbon dioxide and water at 15 kbar and 750°C. The calculated isotopic compositions of water at 15 kbar and 750°C are shown in Table 9.

After calcite was removed from the solid product by acid treatment, the remaining solid was a mixture of quartz and wollastonite. The separation of quartz and wollastonite was not attempted because of the very fine-grained size of the solids and the very small amount of wollastonite in the mixture. The amounts of wollastonite, quartz, and calcite in the solid product can be precisely calculated on the basis of the measurement of the amount of carbon dioxide. Combin-

ing the present fractionation between quartz and water and the fractionation between wollastonite and water by Matthews et al. (1983a), a fractionation of 2.23‰ between quartz and wollastonite at 750°C can be derived. Assuming that quartz and wollastonite reached equilibrium, the calculated isotopic compositions of quartz in the run products are shown in Table 9.

The determination of the isotopic composition of quartz and water involves mass balance calculation. A ±0.5-μmol uncertainty in the measurement of the CO<sub>2</sub> amount causes ±0.1‰ uncertainty in the calculated δ<sup>18</sup>O<sub>water</sub> value. A ±1.0‰ uncertainty in CO<sub>2</sub>-H<sub>2</sub>O fractionation at 750°C and 15 kbar causes ±0.05‰ uncertainty in the calculated δ<sup>18</sup>O<sub>water</sub> value. A ±1.0‰ uncertainty in quartz-wollastonite fractionation causes ±0.06‰ uncertainty in the calculated δ<sup>18</sup>O<sub>quartz</sub> value. Combined with the ±0.1‰ in the measurement of isotopic composition of each phase, the uncertainties for quartz-water and calcite-water fractionations are estimated to be ±0.2‰.

The calculated δ<sup>18</sup>O and δ<sup>17</sup>O values of water, quartz, and the measured values of calcite in the product of run QCW2

Table 6. Oxygen isotopic fractionation between calcite and water at 15 kbar.

Run no.	<i>T</i> (°C)	<i>t</i> (h)	Water	<sup>18</sup> O <sub>MB</sub> <sup>a</sup> (‰)	<sup>18</sup> Δ <sub>f</sub> <sup>b</sup> (‰)	Exchange <sup>c</sup> (%)	<sup>18</sup> Δ <sub>e</sub> <sup>c</sup> (‰)
WCS23	750	72	MEO11	-0.21	0.14	100	
WCS24	750	72	H-H <sub>2</sub> O	-0.21	0.19	100	
WCS25	750	72	MEO11	-0.07	0.22	100	
WCS27	750	72	H-H <sub>2</sub> O	-0.31	0.29	100	
WCS40	750	72	H-H <sub>2</sub> O	-0.19	0.20	100	
						Average	0.21
WCS01	600	72	MEO11	-0.09	0.70	100	
WCS18	600	72	H-H <sub>2</sub> O	-0.17	0.86	100	
WCS05	600	72	MEO11	-0.17	0.84	100	
						Average	0.80
WCS46	500	120	MEO11	0.09	1.73	100	
WCS75	500	120	H-H <sub>2</sub> O	-0.04	1.80	100	
WCS49	500	120	MEO11	-0.10	1.42	100	
						Average	1.65
WCS07	400	240	MEO11	-0.18	2.36	91	
WCS08	400	240	L-H <sub>2</sub> O	-0.01	4.20	91	
WCS41	400	240	MEO11	0.18	2.75	91	
						Average	2.58
WCS11	300	600	MEO11	-0.21	4.31	91	
WCS68	300	600	L-H <sub>2</sub> O	0.04	6.09	91	

Notes a to c are the same as in Table 2.

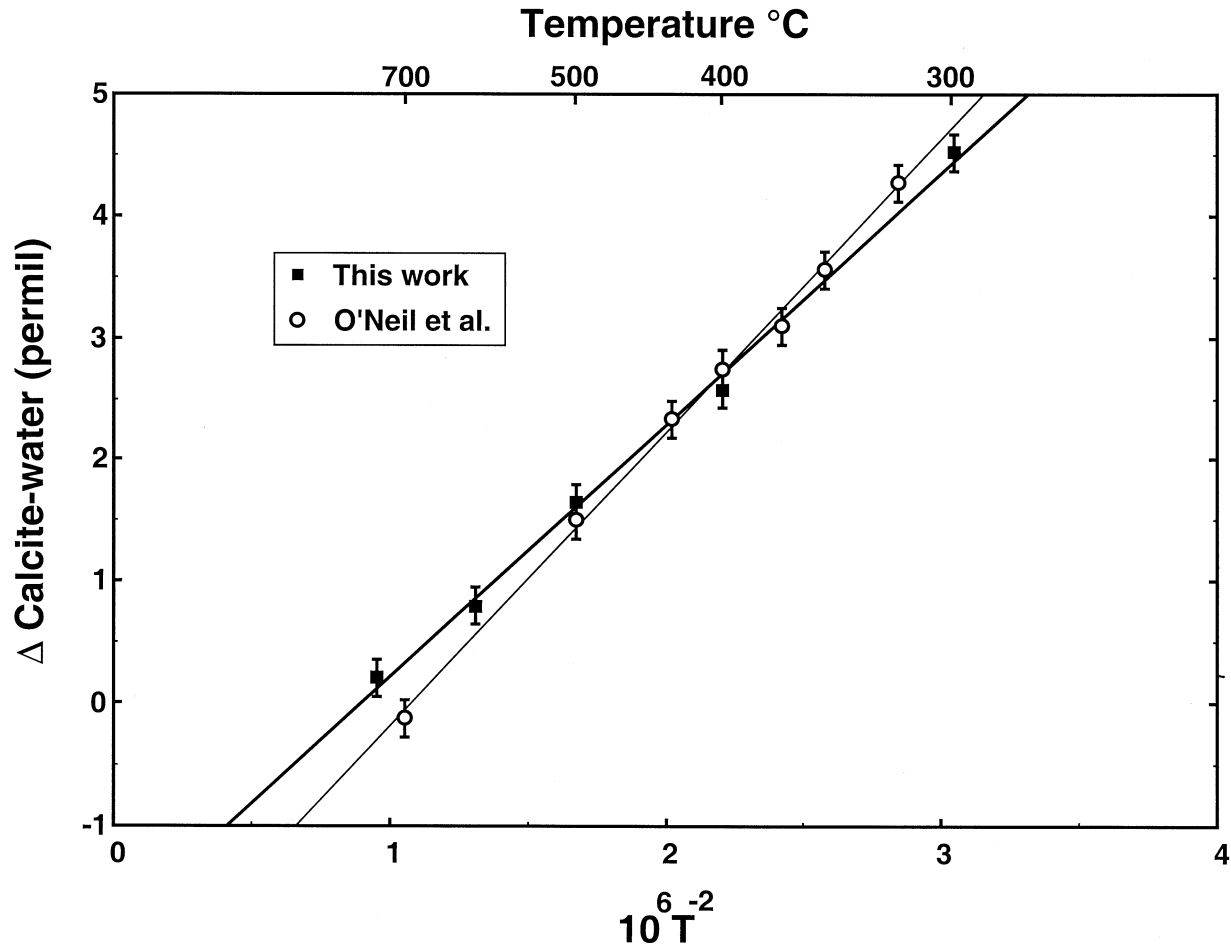


Fig. 3. Isotopic fractionation between calcite and water. The experimental calibration of O'Neil et al. (1969) is shown for comparison.

are shown in Figure 5. All phases in the run products lie on a secondary fractionation line, proving that they have reached isotopic equilibrium. All phases in the product of run QCW1 have same  $\Delta^{17}\text{O}$  ( $\delta^{17}\text{O} - 0.52 \times \delta^{18}\text{O}$ ) values within analytical uncertainty of  $\pm 0.08\text{‰}$ , showing that experiment QCW1 also reached equilibrium.

#### 4.4. Phlogopite-Calcite-Water System

##### 4.4.1. Phlogopite-Water

The results of isotopic fractionation between phlogopite and water are shown in Table 10. The fractionation between phlogopite and water is  $-1.48\text{‰}$  at 15 kbar and  $750^\circ\text{C}$ . Combining the phlogopite-water fractionation and calcite-water fractionation in the present study, a fractionation of  $-1.69\text{‰}$  between phlogopite and calcite by indirect hydrothermal exchange can be derived at 15 kbar and  $750^\circ\text{C}$ .

##### 4.4.2. Phlogopite-Calcite by anhydrous direct exchange

The results of anhydrous direct exchange between phlogopite and calcite at 15 kbar and  $750^\circ\text{C}$  are shown in Table 11.

The reactions reached equilibrium, and the measured fractionation factor of  $-1.68\text{‰}$  is identical to the  $-1.70\text{‰}$  fractionation of the direct exchange result of Chacko et al. (1996).

##### 4.4.3. Phlogopite-Calcite-Water in Three-Phase hydrothermal system

The fractionations among phlogopite, calcite, and water in the three-phase system are shown in Table 12.  $\Delta^{17}\text{O}$  ( $\delta^{17}\text{O} - 0.52 \times \delta^{18}\text{O}$ ) values of all the phases in one run are identical within analytical uncertainty of  $\pm 0.08\text{‰}$ . Shown in Figure 6 as an example is the result of run PCW1. On a three-isotope diagram, all three phases lie on a secondary fractionation line, proving that they reached equilibrium.

In both quartz-calcite-water and phlogopite-calcite-water systems, the determination of isotopic compositions of mineral and water is not affected by the dissolved minerals, as shown by the negligible amount of quench product in SEM images and by the calculation of material balance in each run.

Table 7. Oxygen isotopic fractionation between calcite and NaCl solution at 15 kbar.

Run no.	<i>T</i> (°C)	<i>t</i> (h)	NaCl molality (mol/kg H <sub>2</sub> O)	Water	<sup>18</sup> O <sub>MB</sub> <sup>a</sup> (‰)	<sup>18</sup> Δ <sub>f</sub> <sup>b</sup> (‰)	Exchange <sup>c</sup> (%)	<sup>18</sup> Δ <sub>e</sub> <sup>c</sup> (‰)
WCS26	750	72	6.2	MEOW11	-0.09	0.08	100	
WCS28	750	72	6.2	H-H <sub>2</sub> O	-0.13	0.20	100	
WCS38	750	72	6.2	MEOW11	0.06	0.10	100	
WCS37	750	72	6.2	H-H <sub>2</sub> O	0.03	0.28	100	
							Average	0.17
WCS30	750	72	13.9	MEOW11	-0.09	0.16	100	
WCS29	750	72	13.9	H-H <sub>2</sub> O	-0.27	0.48	100	
WCS31	750	72	13.9	MEOW11	-0.12	0.15	100	
							Average	0.26
WCS32	750	72	23.8	MEOW11	-0.11	0.01	100	
WCS34	750	72	23.8	H-H <sub>2</sub> O	-0.15	0.26	100	
WCS33	750	72	23.8	MEOW11	-0.09	0.27	100	
							Average	0.12
WCS35	750	72	37.0	MEOW11	-0.19	0.21	100	
WCS36	750	72	37.0	L-H <sub>2</sub> O	-0.18	0.38	100	
WCS39	750	72	37.0	MEOW11	0.04	0.07	100	
							Average	0.22
WCS02	600	72	6.2	MEOW11	-0.02	0.67	100	
WCS62	600	72	6.2	H-H <sub>2</sub> O	-0.33	0.87	100	
WCS69	600	72	6.2	MEOW11	0.05	0.60	100	
							Average	0.71
WCS03	600	72	13.9	MEOW11	-0.08	0.60	96	
WCS71	600	72	13.9	H-H <sub>2</sub> O	-0.04	0.08	96	0.61
WCS04	600	72	23.8	MEOW11	-0.13	0.90	100	
WCS74	600	72	23.8	H-H <sub>2</sub> O	-0.15	0.62	100	
WCS78	600	72	23.8	MEOW11	-0.10	0.73	100	
							Average	0.74
WCS47	500	120	6.2	MEOW11	-0.09	1.61	100	
WCS51	500	120	6.2	H-H <sub>2</sub> O	-0.17	1.63	100	
WCS55	500	120	6.2	MEOW11	-0.23	1.34	100	
WCS65	500	120	6.2	MEOW11	0.13	1.53	100	
							Average	1.53
WCS22	500	120	13.9	H-H <sub>2</sub> O	-0.04	1.40	100	
WCS48	500	120	13.9	MEOW11	-0.08	1.44	100	
WCS53	500	120	13.9	H-H <sub>2</sub> O	-0.25	1.46	100	
							Average	1.43
WCS15	400	216	6.2	L-H <sub>2</sub> O	-0.14	4.49	89	
WCS43	400	216	6.2	MEOW11	0.05	2.66	89	2.68
WCS09	400	216	13.9	MEOW11	-0.2	2.59	88	
WCS10	400	216	13.9	L-H <sub>2</sub> O	-0.16	4.59	88	2.61
WCS13	300	600	6.2	MEOW11	-0.21	4.25	87	
WCS14	300	600	6.2	L-H <sub>2</sub> O	0.17	6.36	87	4.51

Notes a to c are the same as in Table 2.

## 5. DISCUSSION

### 5.1. Apparent Oxygen Isotope Salt Effect of NaCl at High Pressure and High Temperature

#### 5.1.1. Apparent Oxygen Isotope Salt Effect of NaCl With Quartz as Reference Mineral

The apparent oxygen isotope salt effect of NaCl measured with quartz as reference phase is  $1000\ln\Gamma_{\text{app NaCl}} = \Delta_{\text{quartz-NaCl solution (quartz)}} - \Delta_{\text{quartz-water (quartz)}}$ . As shown in Figure 2, above 500°C, the apparent oxygen isotope salt effect of NaCl is negative. And its magnitude increases with temperature and with NaCl concentration. The apparent oxygen isotope salt effect of NaCl at 500°C is negligible. At 400°C, the apparent oxygen isotope salt effect of NaCl is positive, and the magnitude increases with NaCl concentration.

The influence of 13.9-molal NaCl on the fractionation between quartz and water at 5 kbar was investigated in this study in an attempt to check whether pressure has an influence on the apparent oxygen isotope salt effect of NaCl. Matsuhisa et al. (1979) and Matthews et al. (1983a) found that although pressure enhanced the exchange rate, it did not change the equilibrium fractionation factor between quartz and water from 400 to 700°C, with pressure ranging from 2 to 20 kbar. Therefore, the fractionation between quartz and water at 15 kbar measured in this study was used as the basis to derive the apparent oxygen isotope salt effect of NaCl at 5 kbar.

At 5 kbar, the apparent oxygen isotope salt effect of 13.9-molal NaCl is -0.60‰ at 600°C and -0.69‰ at 750°C, whereas at 15 kbar, it is -0.20‰ at 600°C and -0.33‰ at 750°C. This shows that pressure has an influence on the ap-

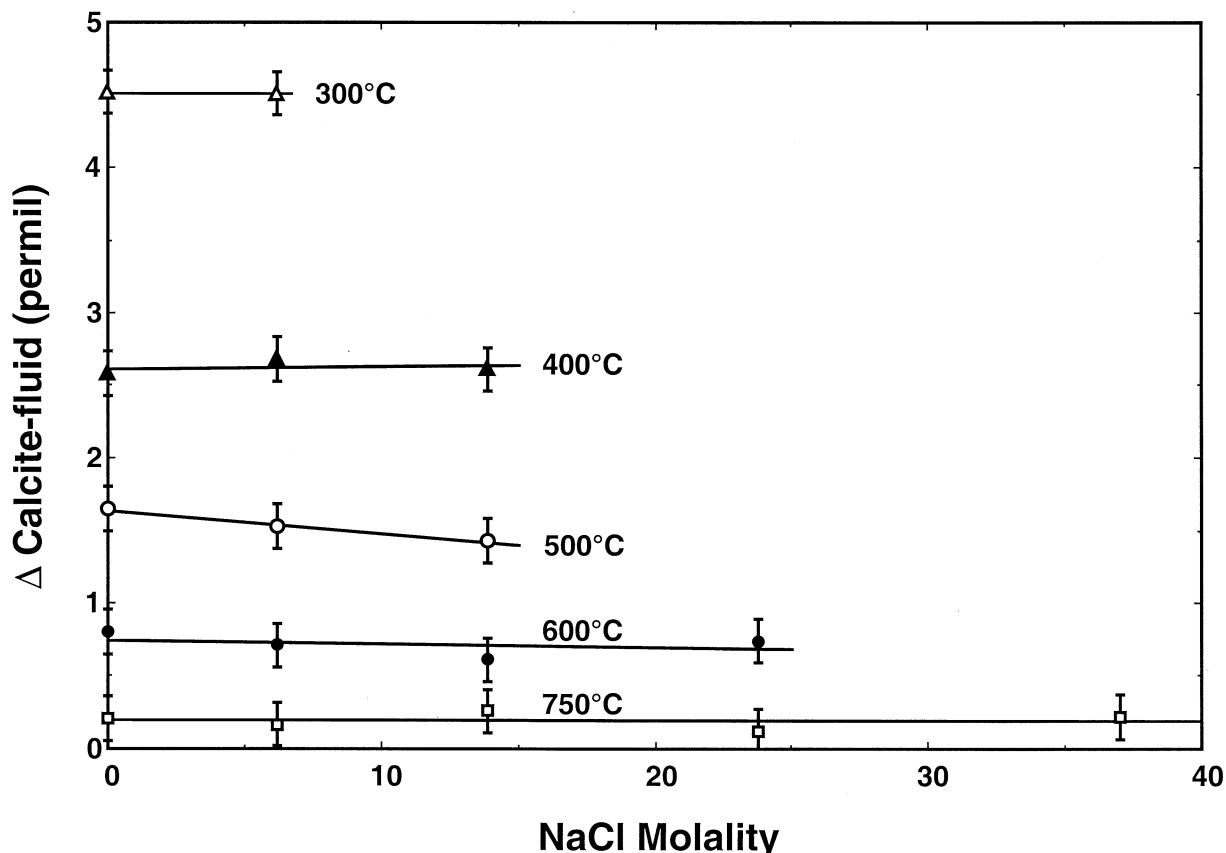


Fig. 4. Isotopic fractionation between calcite and saline solution as a function of NaCl concentration at different temperatures.

parent oxygen isotope salt effect of NaCl, with quartz as the reference phase. At these two temperatures, the magnitude of the apparent oxygen isotope salt effect of NaCl increases slightly with increasing temperature and decreases with increasing pressure.

#### 5.1.2. Apparent oxygen isotope salt effect of NaCl with calcite as reference mineral

In contrast to the change of apparent oxygen isotope salt effect of NaCl with temperature and NaCl concentration observed in quartz-NaCl-water, the apparent oxygen isotope salt effect of NaCl is negligible with calcite as the reference phase at any temperature and NaCl concentration. The largest apparent oxygen isotope salt effect of NaCl measured in the quartz-NaCl-water system is  $-0.85\text{‰}$  for 37-molal NaCl solution at

750°C. The apparent oxygen isotope salt effect of 37-molal NaCl solution at 750°C with calcite as reference phase is  $0.0\text{‰}$ . The  $0.85\text{‰}$  difference in the apparent oxygen isotope salt effects of NaCl between using quartz and calcite as a reference phase is far beyond the analytical uncertainty and cannot be explained by any experimental errors and must relate to the selection of different minerals as reference phases, which will be discussed later.

## 5.2. Oxygen Isotope Salt Effect of Dissolved Minerals

### 5.2.1. Quartz-Calcite-Water system

At 15 kbar and 750°C, the isotopic fractionation between quartz and water is  $1.14\text{‰}$  in the quartz-water system but increases to  $2.42\text{‰}$  in the quartz-calcite-water system. An even

Table 8. Quartz-calcite fractionation by anhydrous direct exchange at 15 kbar and 750°C.

Run no.	$t$ (h)	Initial $\delta^{18}\text{O}_{\text{Qtz}}$ (‰)	Initial $\delta^{18}\text{O}_{\text{Cc}}$ (‰)	Final $\delta^{18}\text{O}_{\text{Qtz}}$ (‰)	Final $\delta^{18}\text{O}_{\text{Cc}}$ (‰)	Final $\Delta^{18}\text{O}_{\text{Qtz-Cc}}$ (‰)	$^{18}\text{O}_{\text{MB}}$ <sup>a</sup> (‰)	Exchange <sup>b</sup> (%)	$^{18}\Delta_e$ <sup>b</sup> (‰)
QC1	288	12.40	14.10	13.60	13.22	0.38	0.16	100	
QC2	288	12.40	17.52	15.28	14.88	0.40	0.12	100	0.39

<sup>a</sup> Material balance calculated by  $^{18}\text{O}_{\text{MB}} = \delta^{18}\text{O}_{\text{mean products}} - \delta^{18}\text{O}_{\text{mean reactants}}$

<sup>b</sup> Equilibrium fractionation factor calculated by method of Northrop and Clayton (1966).

Table 9. Oxygen isotopic fractionation in quartz-calcite-water system at 15 kbar and 750°C.

Run no.		QCW1	QCW2	Average
<i>t</i> (h)		139	145	
Isotopic composition of reactants	$\delta^{18}\text{O}_{\text{Cc}}$ (‰)	14.10	14.10	
	$\delta^{17}\text{O}_{\text{Cc}}$ (‰)	7.34	7.34	
	$\delta^{18}\text{O}_{\text{Qtz}}$ (‰)	12.40	12.40	
	$\delta^{17}\text{O}_{\text{Qtz}}$ (‰)	6.45	6.45	
	$\delta^{18}\text{O}_{\text{H}_2\text{O}}$ (‰)	11.24	11.24	
	$\delta^{17}\text{O}_{\text{H}_2\text{O}}$ (‰)	-3.97	-3.97	
Measured isotopic composition of products	$\delta^{18}\text{O}_{\text{Cc}}$ (‰)	13.43	13.42	
	$\delta^{17}\text{O}_{\text{Cc}}$ (‰)	3.53	3.52	
	$\delta^{18}\text{O}_{\text{Qtz} + \text{Wo}}$ (‰)	13.38	13.52	
	$\delta^{17}\text{O}_{\text{Qtz} + \text{Wo}}$ (‰)	3.47	3.60	
	$\delta^{18}\text{O}_{\text{H}_2\text{O}}$ (‰)	10.22	9.55	
	$\delta^{17}\text{O}_{\text{H}_2\text{O}}$ (‰)	1.89	1.61	
	$\delta^{18}\text{O}_{\text{CO}_2}$ (‰)	51.99	51.34	
$^{18}\text{O}_{\text{MB}}^a$		0.13	0.09	
$^{17}\text{O}_{\text{MB}}^a$		0.03	-0.05	
Isotopic composition of quartz calcite, and water at 750°C and 15 kbar	$\delta^{18}\text{O}_{\text{Qtz}}$ (‰)	13.49	13.66	
	$\delta^{17}\text{O}_{\text{Qtz}}$ (‰)	3.53	3.67	
	$\delta^{18}\text{O}_{\text{Cc}}$ (‰)	13.43	13.42	
	$\delta^{17}\text{O}_{\text{Cc}}$ (‰)	3.53	3.58	
	$\delta^{18}\text{O}_{\text{H}_2\text{O}}$ (‰)	11.28	11.02	
	$\delta^{17}\text{O}_{\text{H}_2\text{O}}$ (‰)	2.45	2.37	
Equilibrium fractionation factors	$^{18}\Delta_{\text{Qtz-H}_2\text{O}}$ (‰)	2.21	2.64	2.42
	$^{18}\Delta_{\text{Cc-H}_2\text{O}}$ (‰)	2.15	2.40	2.27
	$^{18}\Delta_{\text{Qtz-Cc}}$ (‰)	0.06	0.24	0.15

<sup>a</sup> Material balance calculated by  $^{18}\text{O}_{\text{MB}} = \delta^{18}\text{O}_{\text{mean products}} - \delta^{18}\text{O}_{\text{mean reactants}}$ ,  $^{17}\text{O}_{\text{MB}} = \delta^{17}\text{O}_{\text{mean products}} - \delta^{17}\text{O}_{\text{mean reactants}}$ .

larger difference exists between calcite-water fractionations in the calcite-water system and in the quartz-calcite-water system. The difference between the equilibrium fractionation factor for calcite-water in the three-phase hydrothermal system,  $\Delta_{\text{calcite-water (quartz, calcite)}}$ , and the equilibrium fractionation factor for calcite-water in the calcite-water system,  $\Delta_{\text{calcite-water (calcite)}}$ , is caused by the presence of quartz in the three-phase hydrothermal system. The oxygen isotope salt effect of dissolved quartz at 750°C and 15 kbar, therefore, can be obtained by

$$1000\ln\Gamma_{\text{dissolved quartz}} = \Delta_{\text{calcite-water (quartz, calcite)}} \\ -\Delta_{\text{calcite-water (calcite)}} = 2.06\text{‰}.$$

The oxygen isotope salt effect of dissolved calcite at 750°C and 15 kbar is

$$1000\ln\Gamma_{\text{dissolved calcite}} = \Delta_{\text{quartz-water (quartz, calcite)}} \\ -\Delta_{\text{quartz-water (quartz)}} = 1.28\text{‰}.$$

### 5.2.2. Phlogopite-Calcite-Water system

In the quartz-calcite-water system at 15 kbar and 750°C, a kinetic isotope effect may occur in the formation of wollastonite. At 15 kbar and 750°C, no mineralogical reaction was observed between phlogopite and calcite in the hydrothermal system. Therefore, the isotopic fractionation observed in the

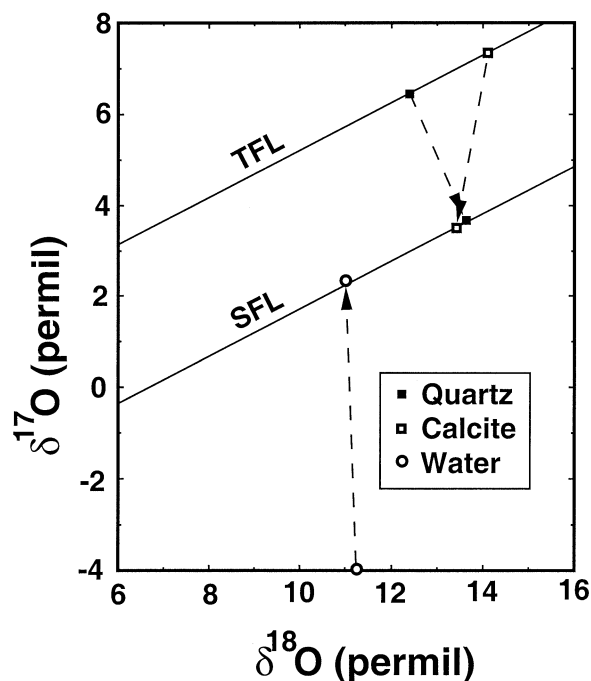


Fig. 5. Isotopic fractionation of run QCW2 of the quartz-calcite-water system. The arrows connect the initial and final compositions of the same phase. It is noted that the arrows do not show the real trajectories of the changes of isotopic compositions during exchange.

phlogopite-calcite-water system is caused only by isotopic exchange. The oxygen isotope salt effect of dissolved phlogopite, therefore, can be obtained by

$$1000\ln\Gamma_{\text{dissolved phlogopite}} = \Delta_{\text{calcite-water (phlogopite, calcite)}} \\ -\Delta_{\text{calcite-water (calcite)}} = 0.69\text{‰},$$

Table 10. Isotopic fractionation between phlogopite and water at 15 kbar and 750°C.

Run no.		PW1	PW2
<i>t</i> (h)		72	72
Isotopic composition of reactants	$\delta^{18}\text{O}_{\text{Phl}}$ (‰)	-8.97	9.56
	$\delta^{17}\text{O}_{\text{Phl}}$ (‰)	-4.66	4.94
	$\delta^{18}\text{O}_{\text{H}_2\text{O}}$ (‰)	11.24	11.24
	$\delta^{17}\text{O}_{\text{H}_2\text{O}}$ (‰)	-3.97	-3.97
Isotopic composition of products	$\delta^{18}\text{O}_{\text{Phl}}$ (‰)	0.43	9.50
	$\delta^{17}\text{O}_{\text{Phl}}$ (‰)	-4.60	0.02
	$\delta^{18}\text{O}_{\text{H}_2\text{O}}$ (‰)	2.19	10.90
	$^{17}\text{O}_{\text{H}_2\text{O}}$ (‰)	-3.86	0.80
$^{18}\text{O}_{\text{MB}}^a$		0.16	-0.20
$^{17}\text{O}_{\text{MB}}^a$		0.11	-0.09
Exchange <sup>b</sup> (‰)		99	100
$\Delta^{18}\text{O}_e^b$ (‰)		-1.57	-1.39

<sup>a</sup> Material balance calculated by  $^{18}\text{O}_{\text{MB}} = \delta^{18}\text{O}_{\text{mean products}} - \delta^{18}\text{O}_{\text{mean reactants}}$ ,  $^{17}\text{O}_{\text{MB}} = \delta^{17}\text{O}_{\text{mean products}} - \delta^{17}\text{O}_{\text{mean reactants}}$ .

<sup>b</sup> Extent of exchange and equilibrium fractionation factor are calculated on the basis of three-isotope method (Matsuhisa et al., 1979).

Table 11. Phlogopite-calcite fractionation by anhydrous direct exchange at 15 kbar and 750°C.

Run no.	<i>t</i> (h)	Initial $\delta^{18}\text{O}_{\text{Phl}}$ (‰)	Initial $\delta^{18}\text{O}_{\text{Cc}}$ (‰)	Final $\delta^{18}\text{O}_{\text{Phl}}$ (‰)	Final $\delta^{18}\text{O}_{\text{Cc}}$ (‰)	$^{18}\text{O}_{\text{MB}}$ <sup>a</sup> (‰)	Exchange (%)	$\Delta^{18}\text{O}_e$ (‰)
PC1	116	9.56	14.1	11.14	12.73	0.12	100	-1.57
PC2	119	-8.97	14.1	1.80	3.49	0.08	100	-1.69
PC3	117	9.56	14.1	10.92	12.72	0.01	100	-1.78
							Average	-1.68

<sup>a</sup> Material balance calculated by  $^{18}\text{O}_{\text{MB}} = \delta^{18}\text{O}_{\text{mean products}} - \delta^{18}\text{O}_{\text{mean reactants}}$ .

and the oxygen isotope salt effect of dissolved calcite in the system of phlogopite-calcite-water is

$$1000\ln\Gamma_{\text{dissolved calcite}} = \Delta_{\text{phlogopite-water (phlogopite, calcite)}} - \Delta_{\text{phlogopite-water (phlogopite)}} = 0.66\text{‰}.$$

The oxygen isotope salt effect of dissolved calcite obtained from the phlogopite-calcite-water system is 0.62‰ smaller than that derived from quartz-calcite-water system, which is beyond the  $\pm 0.28\text{‰}$  uncertainty for  $1000\ln\Gamma_{\text{dissolved calcite}}$  in the quartz-calcite-water system and the  $\pm 0.21\text{‰}$  uncertainty for  $1000\ln\Gamma_{\text{dissolved calcite}}$  in phlogopite-calcite-water. Two possible reasons may cause it: (1) the different solubilities of calcite in the two three-phase systems or (2) the kinetic fractionation associated with the formation of wollastonite in the quartz-calcite-water system.

The initial  $\delta^{17}\text{O}$  values of water and minerals (quartz and calcite) lie on the opposite sides of the secondary fractionation line, as shown in Figure 5. The fact that the isotopic compositions of water and minerals approached from opposite directions and finally having the same  $\Delta^{17}\text{O}$  ( $\delta^{17}\text{O} - 0.52 \times \delta^{18}\text{O}$ ) values indicates that the kinetic fractionation associated with the formation of wollastonite in the quartz-calcite-water system

Table 12. Isotopic fractionation in phlogopite-calcite-water system at 15 kbar and 750°C.

Run no.	PCW1	PCW2	Average	
<i>t</i> (h)	249	70		
Isotopic composition of reactants	$\delta^{18}\text{O}_{\text{Cc}}$ (‰)	14.1	14.1	
	$\delta^{17}\text{O}_{\text{Cc}}$ (‰)	7.34	7.34	
	$\delta^{18}\text{O}_{\text{Phl}}$ (‰)	-8.97	-8.97	
	$\delta^{17}\text{O}_{\text{Phl}}$ (‰)	-4.66	-4.66	
	$\delta^{18}\text{O}_{\text{H}_2\text{O}}$ (‰)	11.24	11.24	
	$\delta^{17}\text{O}_{\text{H}_2\text{O}}$ (‰)	-3.97	-3.97	
Isotopic composition of products	$\delta^{18}\text{O}_{\text{Cc}}$ (‰)	6.66	6.18	
	$\delta^{17}\text{O}_{\text{Cc}}$ (‰)	-0.10	-0.08	
	$\delta^{18}\text{O}_{\text{Phl}}$ (‰)	4.90	4.49	
	$\delta^{17}\text{O}_{\text{Phl}}$ (‰)	-1.09	-0.92	
	$\delta^{18}\text{O}_{\text{H}_2\text{O}}$ (‰)	5.70	5.33	
	$\delta^{17}\text{O}_{\text{H}_2\text{O}}$ (‰)	-0.53	-0.38	
$^{18}\text{O}_{\text{MB}}$ <sup>a</sup>	0.11	-0.17		
$^{17}\text{O}_{\text{MB}}$ <sup>a</sup>	-0.02	-0.01		
Equilibrium fractionation factors	$\Delta^{18}\text{O}_{\text{Phl-H}_2\text{O}}$ (‰)	-0.80	-0.84	-0.82
	$\Delta^{18}\text{O}_{\text{Cc-H}_2\text{O}}$ (‰)	0.95	0.85	0.90
	$\Delta^{18}\text{O}_{\text{Phl-Cc}}$ (‰)	-1.75	-1.68	-1.72

<sup>a</sup> Material balance calculated by  $^{18}\text{O}_{\text{MB}} = \delta^{18}\text{O}_{\text{mean products}} - \delta^{18}\text{O}_{\text{mean reactants}}$ ,  $^{17}\text{O}_{\text{MB}} = \delta^{17}\text{O}_{\text{mean products}} - \delta^{17}\text{O}_{\text{mean reactants}}$ .

should be eliminated in later isotope exchange. Therefore, the difference in the solubility of calcite in the two three-phase systems may be the main reason for the difference in the oxygen isotope salt effects of dissolved calcite measured in these systems.

### 5.3. The Influence of Mineral Dissolution on the Apparent Oxygen Isotope Salt Effect of NaCl

The fractionation between quartz and NaCl solution,  $\Delta_{\text{quartz-NaCl solution (quartz)}}$ , can be expressed as

$$\Delta_{\text{quartz-NaCl solution (quartz)}} = \Delta_{\text{quartz-ion-free water}} + 1000\ln\Gamma_{\text{dissolved quartz (in NaCl solution)}} + 1000\ln\Gamma_{\text{real NaCl}} \quad (9)$$

The fractionation between quartz and water,  $\Delta_{\text{quartz-water (quartz)}}$ , can be expressed as

$$\Delta_{\text{quartz-water (quartz)}} = \Delta_{\text{quartz-ion-free water}} + 1000\ln\Gamma_{\text{dissolved quartz (in water)}} \quad (10)$$

Therefore, the apparent isotope salt effect of NaCl, with quartz as the reference phase, is

$$1000\ln\Gamma_{\text{app NaCl}} = \Delta_{\text{quartz-NaCl solution (quartz)}} - \Delta_{\text{quartz-water (quartz)}} = (1000\ln\Gamma_{\text{dissolved quartz (in NaCl solution)}} - 1000\ln\Gamma_{\text{dissolved quartz (in water)}}) + 1000\ln\Gamma_{\text{real NaCl}} \quad (11)$$

The isotope salt effect of quartz in water at 15 kbar and 750°C is +2.06‰. At 15 kbar, the presence of NaCl decreases the solubility of quartz (Newton and Manning, 2000). If the magnitudes of the oxygen isotope salt effect of dissolved minerals increase with mineral solubilities, then the oxygen isotope salt effect of dissolved quartz in water,  $1000\ln\Gamma_{\text{dissolved quartz (in water)}}$ , will be more positive than that in NaCl solution,  $1000\ln\Gamma_{\text{dissolved quartz (in NaCl solution)}}$ . The net contribution of the isotope salt effect of dissolved quartz to the apparent isotope salt effect of NaCl

$$\Delta\Gamma_{\text{net dissolved quartz}} = 1000\ln\Gamma_{\text{dissolved quartz (in NaCl solution)}} - 1000\ln\Gamma_{\text{dissolved quartz (in water)}}$$

should be negative. The apparent oxygen isotope salt effect of NaCl is the sum of the real isotope salt effect of NaCl and the net contribution of the isotope salt effect of dissolved quartz. The net contribution of the isotope salt effect of dissolved quartz has the same sign as the apparent oxygen

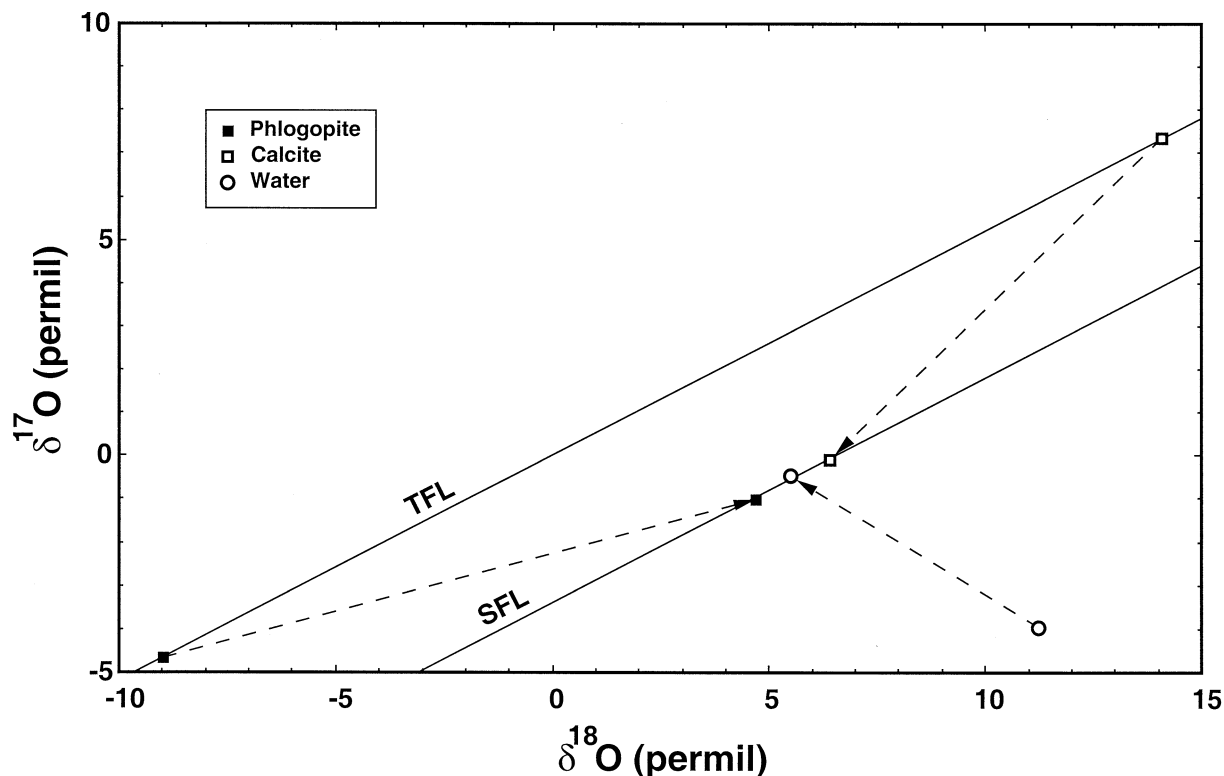


Fig. 6. Isotopic fractionation in run PCW2 of the phlogopite-calcite-water system. The arrows connect the initial and final compositions of the same phase. It is noted that the arrows do not show the real trajectories of the changes of isotopic compositions during exchange.

isotope salt effect of NaCl, and the magnitude of the apparent oxygen isotope salt effect of NaCl is small at high pressure and high temperature. This implies that the real oxygen isotope salt effect of NaCl at 15 kbar is either very small or is positive.

Below 2 kbar, at fixed temperature and pressure, the solubility of calcite always increases with NaCl concentration (Malinin and Kanukov, 1971; Fein and Walther, 1989). It is not known how the presence of NaCl influences the solubility of calcite under high pressure. If NaCl affects the solubility of calcite, a net contribution of oxygen isotope salt effect of dissolved calcite will be added to the apparent oxygen isotope salt effect of NaCl measured with calcite as reference phase, following the same reasoning for the apparent isotope salt of NaCl with quartz as reference phase.

Under high pressure and high temperature, the use of a mineral as a reference phase may not derive real isotope salt effects of solutes if the solutes change the solubility of the reference mineral. Therefore, the apparent oxygen isotope salt effect of NaCl measured at high temperature and high pressure may not be comparable to that measured at low pressure and low temperature with simple extrapolation. The net contributions of oxygen isotope salt effects of dissolved quartz and calcite may cause the systematic difference in the apparent oxygen isotope salt effects of NaCl in the quartz-NaCl-water and calcite-NaCl-water systems.

#### 5.4. Apparent Oxygen Isotope Salt Effect of CaCl<sub>2</sub>

The apparent oxygen isotope salt effect of 5-molal CaCl<sub>2</sub> measured at 15 kbar with quartz as reference phase is  $-0.68\text{‰}$  at 600°C and  $-0.61\text{‰}$  at 750°C. The oxygen isotope salt effect of CaCl<sub>2</sub> at room temperature and 1 atm is quite large. The regression of the results of Sofer and Gat (1972), Truesdell (1974), and O'Neil and Truesdell (1991) yields a coefficient of  $-0.50\text{‰}/\text{mol/L}$  for the linear relation between oxygen isotope salt effect and the molality of CaCl<sub>2</sub> at 25°C. From 50 to 100°C, the oxygen isotope salt effect of CaCl<sub>2</sub> is negative; its magnitude increases linearly with CaCl<sub>2</sub> concentration and decreases slightly with increasing temperature (Horita et al., 1993a). The magnitude of the apparent oxygen isotope salt effect of 5-molal CaCl<sub>2</sub> at 15 kbar and 600°C is identical to that at 750°C within analytical uncertainty. Therefore, the temperature dependence of the apparent oxygen isotope salt effect of CaCl<sub>2</sub> at high pressure and high temperature is not clear.

The magnitude of the apparent oxygen isotope salt effect of CaCl<sub>2</sub> at 15 kbar at 600 and 750°C is much smaller than that at low pressure and low temperature. It is not known whether the tendency of slight decrease of magnitude with the increase of temperature observed by Horita et al. (1993a) below 100°C extends to high temperature. The small oxygen isotope salt effect of CaCl<sub>2</sub> at high pressure and high temperature observed in this study could be caused by the changes of temperature and

pressure and the net contribution of the oxygen isotope salt effect of dissolved quartz.

### 5.5. The Influences of Ionic Charge and Type on the Oxygen Isotope Salt Effects

Isotope salt effects in aqueous solutions can be ascribed to the interaction between water molecules and solutes. Ionic charge and ionic radius affect the interaction between ions and water molecules and thus affect isotope salt effects. Sofer and Gat (1972) observed a linear relation between isotope salt effects and the ionic parameter  $q/r$ , where  $q$  is ionic charge and  $r$  is ionic radius, at 25°C. Horita et al. (1993a) found that below 100°C, the magnitudes of the oxygen isotope salt effects of divalent cations are much larger than those of monovalent cations.

Direct comparison can be made between the apparent oxygen isotope salt effect of NaCl and CaCl<sub>2</sub> at high pressure and high temperature measured in this study. Assuming that the apparent oxygen isotope salt effect of NaCl varies linearly with concentration at 600 and 750°C, the derived apparent oxygen isotope salt effects in 5-molal NaCl at 600 and 750°C are -0.08 and -0.13‰, respectively, while the apparent oxygen isotope salt effect of 5-molal CaCl<sub>2</sub> is -0.68‰ at 600°C and -0.61‰ at 750°C. The apparent oxygen isotope salt effect of 5-molal CaCl<sub>2</sub> is larger than the apparent oxygen isotope salt effect of 5-molal NaCl at both temperatures. Because the influence of CaCl<sub>2</sub> on the solubility of quartz under our experimental conditions is not known, the net contribution of oxygen isotope salt effect of dissolved quartz to the apparent oxygen isotope salt effect of CaCl<sub>2</sub> is not known. It is also not known how anions affect mineral-water fractionation. Therefore, it is tentatively suggested that a solute with a divalent cation also has a larger oxygen isotope salt effect than a solute with a monovalent cation at high pressure and high temperature.

On the basis of their study of isotope salt effects at pressures and temperatures that are much lower than in the present study, Horita et al. (1993) proposed that the oxygen isotope salt effects are controlled largely by the type and concentration of cations because cations interact more strongly with the dipole of the water molecule than do anions. CaCl<sub>2</sub> and calcite have the same cation. Although the apparent oxygen isotope salt effect of CaCl<sub>2</sub> is negative, the oxygen isotope salt effect of dissolved calcite is positive, and the magnitude is significant. This might be caused by the contribution of oxygen isotope salt effect of dissolved quartz to the apparent oxygen isotope salt effect of CaCl<sub>2</sub> or, alternatively, suggests that the anion may produce a measurable oxygen isotope salt effect at high pressure and high temperature.

### 6. OXYGEN ISOTOPE SALT EFFECTS OF DISSOLVED MINERALS AND THE CALIBRATION OF OXYGEN ISOTOPE THERMOMETERS

The fractionation between two minerals in the three-phase hydrothermal system can be regarded as the real fractionation between them because the two minerals exchange oxygen isotopes with the same medium in a closed system. This provides a criterion by which to judge whether hydrothermal indirect exchanges or anhydrous carbonate exchanges provide the correct fractionation for a mineral pair.

At 15 kbar and 750°C, the fractionation between quartz and calcite measured in the system of quartz-calcite-water is 0.15‰. This is somewhat smaller than the fractionation of 0.39‰ obtained by anhydrous direct exchange between the two minerals, although considering the  $\pm 0.15\%$  analytical uncertainty, the two values are identical. Combining quartz-water fractionation in quartz-water system and calcite-water fractionation in calcite-water system, a fractionation factor of 0.93‰ between quartz and calcite can be derived from the hydrothermal indirect exchanges at 15 kbar and 750°C. This value is much larger than that measured in the three-phase hydrothermal system. This suggests that the combination of indirect mineral-water fractionations to yield a mineral-mineral fractionation can lead to errors when the isotope salt effects of the two minerals are not the same under the experimental conditions.

Sharp and Kirschner (1994) calibrated the quartz-calcite oxygen isotope thermometer on the basis of measured  $\Delta^{18}\text{O}_{\text{quartz-calcite}}$  values from natural samples. Their empirical calibration gives a fractionation of 0.83‰ between quartz and calcite at 750°C. This value is also much larger than the fractionation measured in the three-phase hydrothermal system and in the anhydrous system.

The quartz-calcite fractionation obtained by indirect hydrothermal exchange at 15 kbar and 750°C is 0.93‰, which has the same sign and magnitude as the 0.78‰ difference between the oxygen isotope salt effect of dissolved quartz and that of dissolved calcite, within analytical uncertainty. This strongly suggests that the discrepancy between fractionations for quartz-calcite obtained by hydrothermal indirect exchanges and that by anhydrous direct exchanges is caused by the difference between the oxygen isotope salt effect of dissolved quartz and that of dissolved calcite.

At 15 kbar and 750°C, the agreement between the direct hydrothermal exchange result and anhydrous direct exchange result for phlogopite-calcite pair is very good. However, unlike the quartz-calcite pair, which shows a large discrepancy between the direct and the indirect hydrothermal exchange results, the fractionation for the phlogopite-calcite pair obtained by indirect hydrothermal exchange is in excellent agreement with the result of direct hydrothermal exchange. This apparent agreement is the consequence of equal oxygen isotope salt effects of dissolved phlogopite and dissolved calcite. At 15 kbar and 750°C, the oxygen isotope salt effect of dissolved phlogopite is 0.69‰, and the isotope salt effect of dissolved calcite is 0.66‰. Therefore, they cancel each other in the indirect hydrothermal exchange.

In both the quartz-calcite-water system and the phlogopite-calcite-water system, the differences between the oxygen isotope salt effect of dissolved silicate and that of dissolved calcite have the same sign and magnitude as the differences between the fractionation for the silicate-calcite pair obtained by hydrothermal indirect exchange and that obtained by anhydrous direct exchange. This shows that the discrepancies in fractionations for pairs of minerals obtained by hydrothermal indirect exchange and by carbonate exchange are due to the differences in the oxygen isotope salt effects of dissolved minerals.

The isotopic exchange experiments in anhydrous systems that consist of calcite and another mineral do not suffer the influence of oxygen isotope salt effects and thus eliminate the



source of error produced by the different isotope salt effects of dissolved minerals. Carbonate exchanges provide the same fractionations for quartz-calcite and phlogopite-calcite pairs as those measured in three-phase hydrothermal systems. This indicates that oxygen isotope fractionation calibrated by carbonate exchange method is reliable because anhydrous exchange experiments use an identical exchange medium (i.e., carbonate), and fractionations may be combined from different mineral-carbonate experiments (Clayton and Kieffer, 1991).

### 7. OXYGEN ISOTOPE SALT EFFECTS AND THE ESTIMATION OF OXYGEN ISOTOPE COMPOSITION OF FOSSIL AQUEOUS FLUIDS

Oxygen isotope compositions of paleo aqueous fluids are usually derived from the isotopic composition of a mineral and the fractionation between the mineral and the aqueous fluid. It is assumed that the mineral and aqueous fluid were in isotopic equilibrium, and the temperature of equilibration is known independently. However, it has been observed that experimental calibrations of mineral-water fractionations are systematically 1.5 to 2.0‰ more positive than the theoretical calculations (Bottinga, 1968; Clayton et al., 1989) at high temperature. This creates some uncertainties in the estimation of oxygen isotope compositions of paleo aqueous fluids based on mineral-water fractionations.

The fractionation between a mineral and water can be expressed as

$$\Delta_{\text{mineral-water (mineral)}} = \Delta_{\text{mineral-ion-free water}} + 1000\ln\Gamma_{\text{dissolved mineral}} \quad (12)$$

In theoretical calculations (Bottinga, 1968; Bottinga and Javoy, 1973), the interaction between water molecules and species of dissolved minerals was not considered. The calculated fractionation between a mineral and water may be represented by the term  $\Delta_{\text{mineral-ion-free water}}$ . Therefore, the difference in experimentally calibrated fractionation between a mineral and water and that obtained by theoretical calculation may be mainly caused by the isotope salt effect of the dissolved mineral and isotope pressure effects on mineral and water. If this is correct, the larger the oxygen isotope salt effect of a mineral, the larger the difference in mineral-water fractionations obtained by experimental calibration and by theoretical calculation. As mentioned above, the discrepancies in mineral-calcite fractionations obtained by indirect hydrothermal exchange and by carbonate exchange is caused by the difference in their isotope salt effects. The larger the isotope salt effect of a mineral, the larger the discrepancy in the mineral-calcite fractionation between indirect hydrothermal exchange and carbonate exchange. Therefore, the difference between experimental and calculated mineral-water fractionations should correlate with the discrepancies in the mineral-calcite fractionations between indirect hydrothermal exchange and carbonate exchange.

Such a correlation is shown in Figure 7. The measured slope of the correlation is 0.92, with an  $r^2$  value of 0.97, implying that the same phenomenon causes both effects. This strongly supports the reality of the isotope salt effect of dissolved minerals and the proposal that isotope salt effects of dissolved minerals in experiments contribute to the difference between experimental mineral-water fractionations and theoretical calculations.

It should be emphasized that the isotope salt effect of dissolved mineral,  $1000\ln\Gamma_{\text{dissolved mineral}}$ , is not the same as the mineral/water term,  $1000\ln\beta_{\text{mineral/water}}$ , in the increment method of Zheng (1993). The mineral/water term in the increment method cannot describe the isotope salt effect of a dissolved mineral, because this term somehow reflects the cation-oxygen bond strength (composition and structure) of a mineral. However, the isotope salt effect of dissolved mineral is controlled by the solute-water interaction, which is a function of solute concentration (mineral solubility), solute species, and hydration (numbers), which are in turn controlled by pressure and temperature.

Rosenbaum (1997) derived reduced partition function ratios of supercritical water on the basis of experiments of mineral-water fractionations. Because of the presence of oxygen isotope salt effects of dissolved minerals in experimental studies and the magnitudes of isotope salt effects of different minerals are different, the reduced partition function ratios of supercritical water he derived are in error by 1 to 2‰ at high temperature.

The oxygen isotope salt effects of most minerals are on the order of 1 to 2‰, inferred from the differences in experimental mineral-water fractionations and theoretical calculations as shown in Figure 7. The comparison of experimental and calculated albite-water fractionations by Clayton et al. (1989) suggested that the 1 to 2‰ oxygen isotope salt effects of dissolved minerals might also exist at temperature as low as 300°C. The isotopic fractionation factor between water and a mineral in a multimineral hydrothermal system may be larger than that measured in a two-phase hydrothermal system consisting of only water and the mineral by at least 1 to 2‰ because of the contribution of the oxygen isotope salt effects of other coexisting minerals. As a result, at high temperature, the isotopic compositions of fossil fluids estimated on the basis of two-phase hydrothermal fractionations may be overestimated by at least +1 to +2‰.

### 8. CONCLUSIONS

Differences of isotope salt effects of dissolved minerals are the reason for the discrepancies between fractionations of pairs of minerals obtained by indirect hydrothermal exchange and by carbonate exchange. The use of calcite as exchange medium in the calibration of oxygen isotope thermometry eliminates the source of error produced by the difference in isotope salt effects of dissolved minerals. Therefore, the carbonate exchange technique provides more accurate results for the construction of mineral-pair oxygen isotope thermometers.

The oxygen isotope salt effects of dissolved minerals in experimental studies are the main reason for the discrepancy between the experimentally calibrated mineral-water fractionation and the calculated mineral-water fractionation. In natural systems, aqueous fluids normally equilibrate with several minerals. When deriving isotopic compositions of geological aqueous fluids on the basis of the fractionation factor between water and one mineral, the isotope salt effects of other coexisting minerals should be considered. The isotope salt effects of several common minerals are on the order of +1 to +2‰. Consequently, at high temperature, the oxygen isotope compositions of fossil fluids estimated from two-phase hydrothermal experiments may be overestimated by at least +1 to +2‰.

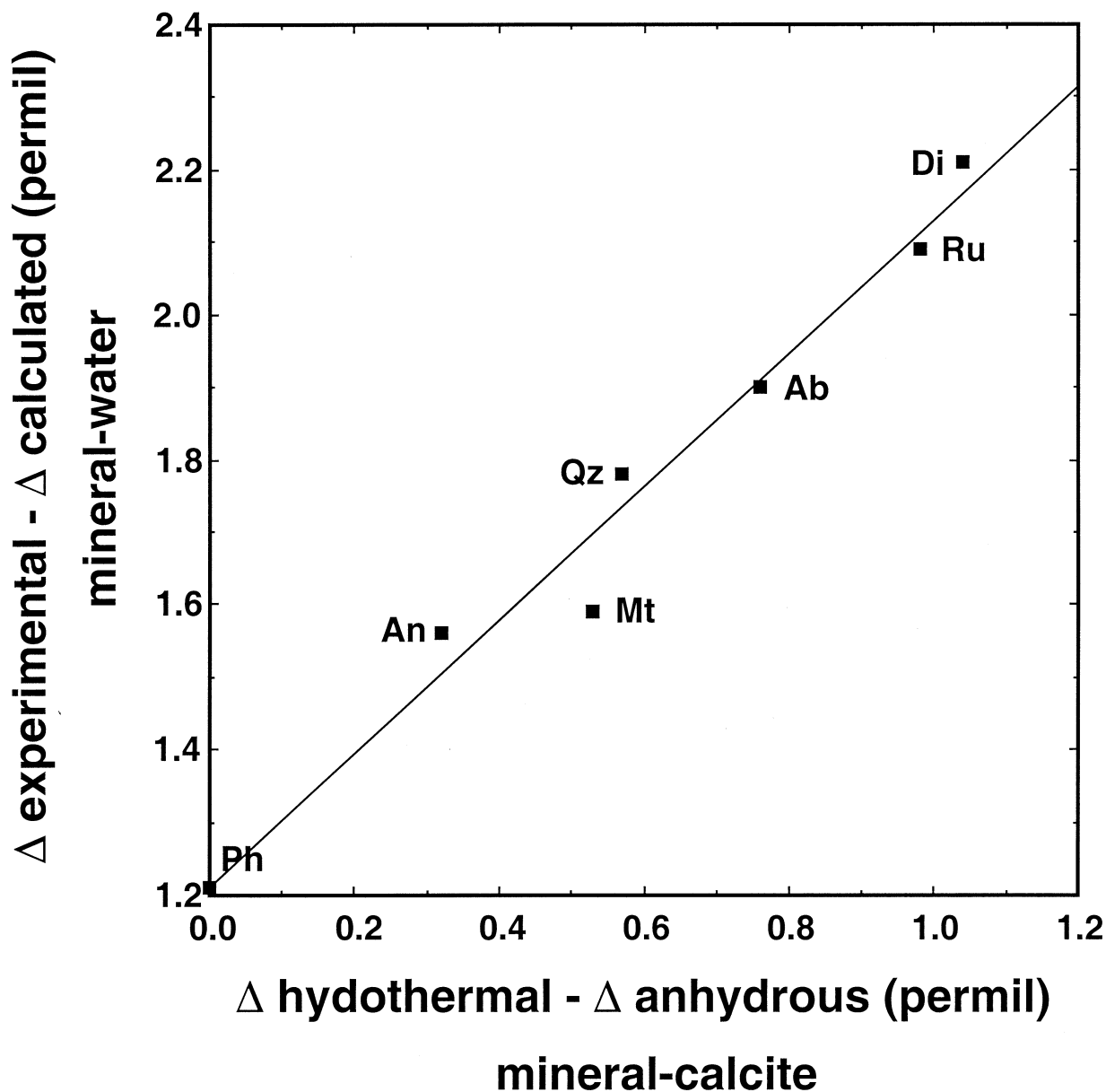


Fig. 7. Comparison of discrepancies in mineral-calcite fractionations and the differences in mineral-water fractionations at 750°C. Phl = phlogopite, An = anorthite, Mt = magnetite, Qz = quartz, Ab = albite, Rt = rutile, Di = diopside. Sources for mineral-water fractionation: quartz, calcite, phlogopite (this study); albite and anorthite (Matsuhisa et al., 1979); magnetite (O'Neil, 1963); diopside (Matthews et al., 1983b); rutile (Addy and Garlick, 1974). Sources for anhydrous mineral-calcite fractionation: quartz, albite, anorthite (Clayton et al., 1989); diopside and magnetite (Chiba et al., 1989); rutile (Chacko et al., 1996). The reduced partition function ratios of water are from Bottinga and Javoy (1973). Sources for the partition function ratios for minerals are albite, anorthite, diopside, magnetite, and quartz from Clayton and Kieffer (1991), phlogopite and rutile from Chacko et al. (1996).

NaCl has different influences on quartz-water fractionation and calcite-water fractionation. The apparent isotope salt effect of NaCl measured with quartz and calcite as reference phase consists of the real isotope salt effect of NaCl and a net contribution of oxygen isotope salt effects of the fraction of dissolved minerals caused by the changes of solubilities compared to those in pure water. Real oxygen isotope salt effects of solutes cannot be measured with a mineral as reference if the presence of the solutes changes the solubility of the mineral.

At high pressure and high temperature, a solute with divalent

cation may have larger oxygen isotope salt effect than a solute with monovalent cation. Anions may also have measurable oxygen isotope salt effects at high pressure and high temperature.

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**Appendix.** Discrepancies Between Mineral-Pair Fractionations Obtained by Indirect Hydrothermal Exchange and Carbonate Exchange

Mineral pair <sup>a</sup>	$\frac{\Delta_{\text{hydrothermal exchanges}} - \Delta_{\text{carbonate exchanges}}}{\text{exchanges}} (\text{‰})$			Data sources <sup>b</sup>
	700 (°C)	600 (°C)	500 (°C)	
Qz-Cc	0.82	0.70	0.28	Matsuhisa et al. (1979), Clayton et al. (1989)
Ab-Cc	1.29	1.24	0.98	Matsuhisa et al. (1979), Clayton et al. (1989)
An-Cc	0.91	1.15	0.90	Matsuhisa et al. (1979), Clayton et al. (1989)
Di-Cc	1.50	1.64		Matthews et al. (1983b), Chiba et al. (1989)
Mt-Cc	0.89			Matthews et al. (1983b), Chiba et al. (1989)
Di-Ab	0.21	0.40		Matthews et al. (1983b), Matsuhisa et al. (1979), Clayton et al. (1989), Chiba et al. (1989)
Di-An	0.59	0.49		Matthews et al. (1983b), Matsuhisa et al. (1979), Clayton et al. (1989), Chiba et al. (1989)
Di-Qz	0.68	0.94		Matthews et al. (1983b), Matsuhisa et al. (1979), Clayton et al. (1989), Chiba et al. (1989)
Ab-Qz	0.47	0.54	0.70	Matsuhisa et al. (1979), Clayton et al. (1989)

<sup>a</sup> Qz = quartz, Cc = calcite, Ab = albite, An = anorthite, Di = diopside, Mt = magnetite.

<sup>b</sup> Calcite-water fractionations are from O'Neil et al. (1969).