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Oxygen isotope exchange and disequilibrium between calcite and tremolite in the absence and presence of an experimental C–O–H fluid

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Abstract Oxygen isotope exchange between minerals during metamorphism can occur in either the presence or the absence of aqueous fluids. Oxygen isotope partitioning among minerals and fluid is governed by both chemical and isotopic equilibria during these processes, which progress by intragranular and intergranular diffusion as well as by surface reactions. We have carried out isotope exchange experiments in two- and three-phase systems, respectively, between calcite and tremolite at high temperatures and pressures. The two-phase system experiments were conducted without fluid either at 1 GPa and 680 °C for 7 days or at 500 MPa and 560 °C for 20 days. Extrapolated equilibrium fractionations between calcite and tremolite are significantly lower than existing empirical estimates and experimental determinations in the presence of small amounts of fluid, but closely match calculated fractionations by means of the increment method for framework oxygen in tremolite. The small fractionations measured in the direct calcite–tremolite exchange experiments are interpreted by different rates of oxygen isotope exchange between hydroxyl oxygen, framework oxygen and calcite during the solid–solid reactions where significant recrystallization occurs. The three-phase system experiments were accomplished in the presence of a large amount of fluid (CO₂ + H₂O) at 500 MPa and 560 °C under conditions of phase equilibrium for 5, 10, 20, 40, 80, 120, 160, and 200 days. The results show that oxygen isotope exchange between minerals and fluid proceeds in two stages: first, through a mechanism of dissolution-

recrystallization and very rapidly; second, through a mechanism of diffusion and very slowly. Synthetic calcite shows a greater rate of isotopic exchange with fluid than natural calcite in the first stage. The rate of oxygen diffusion in calcite is approximately equal to or slightly greater than that in tremolite in the second stage. A calculation using available diffusion coefficients for calcite suggests that grain boundary diffusion, rather than volume diffusion, has been the dominant mechanism of oxygen transport between the fluid and the mineral grains in the later stage.

Introduction

Oxygen isotope analysis of minerals has been widely used to quantify fluid–rock interactions in hydrothermal alteration and metamorphic processes (e.g., Valley et al. 1986; Hoefs 1997; Zheng et al. 2003). It is well known that different minerals exhibit varying susceptibilities to isotopic exchange, resulting in isotopic disequilibrium among minerals even at high temperatures (e.g., Criss and Taylor 1983; Gregory et al. 1989). Furthermore, the mechanisms of isotopic exchange are variable and can include chemical reactions, dissolution–recrystallization and diffusion, depending on the geochemical conditions (e.g., fluid and mineral chemistry, temperature, and pressure) at the time of the interaction (Cole et al. 1983; Matthews et al. 1983a; Giletti 1985; Hu and Clayton 2003). The mobility of oxygen-bearing species, as identified by oxygen isotope exchange experiments, provides unique insights into the nature of fluid–rock interactions. Volume diffusion through a crystal lattice is often the rate-limiting step in oxygen isotope exchange between minerals. In contrast, diffusion through a fluid, along a grain boundary, or on a surface is more rapid. Grain boundaries are significant pathways for oxygen isotope exchange, especially if they are hydrated, discordant, or filled with hydrous alteration or fluid. As a result, the grain

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boundary diffusion may be replaced by surface reactions such as dissolution-precipitation during the process of fluid–mineral interactions.

Knowledge of the kinetics of fluid and chemical migration through rocks is of fundamental importance to geologists. A great deal of experimental determinations has been devoted to the rate and mechanism of oxygen isotope exchange between single mineral and fluid. Most rocks, however, are not monomineralic in nature, and there are numerous indirect observations and suggestions in the geological literature that oxygen isotope exchange between minerals in the presence of fluid may be significantly different from that between single mineral and fluid. Cole et al. (1992) carried out kinetic experiments of oxygen isotope exchange between granitic minerals and water under hydrothermal conditions. However, the occurrence of alteration minerals in their exchanged products complicated the interpretation of the isotopic data. The exchange experiments of Zheng et al. (1999) in the system calcite–forsterite–H₂O–CO₂ at 680 °C and 500 MPa under conditions of phase equilibrium yielded disequilibrium fractionation of oxygen isotopes. It appears that the disequilibrium fractionation arose because calcite and forsterite exchange oxygen isotopes at different rates with fluid. In addition, even if the solid/fluid ratio was low, the oxygen isotope composition of the fluid changed in the course of the experiments, potentially allowing isotopic zoning to develop in mineral overgrowths. Thus, the oxygen isotope exchange between minerals in the presence of a large amount of fluid is different from two-phase mineral–fluid systems.

On the other hand, oxygen isotope exchange between calcite and silicate in the presence of small quantities of supercritical CO₂–H₂O fluid under conditions of phase equilibrium was successfully employed to calibrate the fractionation factors between forsterite, tremolite and calcite (Zheng et al. 1994a, 1994b). With respect to fractionation factor calibration by exchange experiments, there are currently two large sets of data on oxygen isotope fractionation factors between minerals, one obtained using fluid (H₂O or H₂O + CO₂), and the other using carbonate as the isotopic exchange medium. With respect to mineral-pair fractionation factors derived from the two sets, however, some of them agree with each other but some not (Chacko 1993; Matthews 1994; Hu and Clayton 2003), and some of them are in agreement with empirical calibrations but some not (Zheng 1999). It appears that knowledge of the rates and mechanisms of isotopic exchange between minerals in the presence of fluid is critical to the interpretation of isotopic equilibration in natural and experimental mineral assemblages. This paper presents the results of an experimental study on the oxygen isotope exchange between calcite and tremolite in the presence of a large amount of C–O–H fluid and without fluid. The results provide insight into the process and mechanism of isotopic exchange concerning hydroxyl-bearing minerals.

Experimental methods

Two different calcites were used as the starting materials in the second type of experiments, one of which was derived from chemical synthesis (A) and the other from a natural carbonatite (B). A third calcite, also of synthetic origin, was employed in the first type of anhydrous experiments. A natural tremolite from Nord Talgje in southern Norway (Mueller and Strauss 1984) was used as the common starting material. The tremolite had the following compositions (wet chemical analysis, weight%): 57.5 SiO₂, 0.14 TiO₂, 1.4 Al₂O₃, 0.8 FeO, 24.0 MgO, 12.85 CaO, 0.36 Na₂O, 0.11 K₂O, 0.21 F and 2.0 H₂O (Dachs and Metz 1988). Microprobe analyses revealed that the tremolite was generally homogeneous but sometimes contained cores in which FeO and Al₂O₃ were slightly enriched. Mineral inclusions of quartz, calcite or talk were occasionally observed in tremolite under the microscope, but free of fluid inclusions. The CO₂ was acquired by the thermal decomposition of Ag₂C₂O₄.

Oxygen isotope equilibrium was approached from opposite directions by an appropriate choice of the $\delta^{18}\text{O}$ value of the starting materials. The isotopic composition of the starting materials is listed in Table 1. The solid charge was loaded together with the fluid charge into a capsule made from gold tubing. During sealing (arc welding) the lower part of the capsule was cooled by a water–NaCl–ice mixture. The charged capsules were weighed not only before and after sealing but also before and after runs in order to ensure the quality of sealing. Two types of exchange experiments were carried out between calcite and tremolite.

The first type was conducted in a two-phase system for two sets of companion experiments without fluid, either in a piston-cylinder apparatus at 1 GPa and 680 °C for 7 days using a NaCl pressure cell, or in standard cold-seal pressure vessels (conventional hydrothermal autoclaves) at 500 MPa and 560 °C for 20 days using CO₂ as the pressure medium. Uncertainties in the temperature and pressure measurements were ± 5 °C and ± 5 MPa, respectively. Because isotopic exchange was not complete in the experiments, extrapolations to equilibrium fractionation were made using the approach of Northrop and Clayton (1966). The experimental method follows the procedures of Clayton et al. (1989) and Chiba et al. (1989) for calibrating oxygen isotope fractionation factors between calcite and anhydrous silicates. Similar experiments were carried out by Chacko et al. (1996) for muscovite and phlogopite.

The second type was accomplished in three-phase systems in the cold-seal vessels at 500 MPa and 560 °C in the presence of a large amount of fluid (CO₂+H₂O) for 5, 10, 20, 40, 80, 120, 160, and 200 days. The sample was quenched by removing the vessel from the furnace and quickly cooling it with compressed air. As shown in Fig. 1, the experiments were performed in the T – P – X_{CO_2} stability field of the calcite–tremolite assemblage, on the basis of the experimental petrological data summarized by Metz (1983) and thermodynamic calculations by Gottschalk (1997). The fluid was a mixture of H₂O and CO₂, the mole fraction of CO₂ being 0.4. The weight proportion of CO₂ to H₂O was chosen such as to maintain the stability of the calcite–tremolite assemblage at the experimental temperature and pressure. The experimental methodology closely follows that of

Table 1 Isotopic composition of starting materials

Material	Origin	$\delta^{18}\text{O}_{\text{SMOW}}$ (‰)	$\delta^{13}\text{C}_{\text{PDB}}$ (‰)
Calcite	Synthetic (Merck)	18.65	–22.37
Calcite	Synthetic (p.A.)	15.41	–7.29
Calcite	Natural (NBS-28)	7.84	–5.13
Tremolite	Natural	11.52	
CO ₂	Ag ₂ C ₂ O ₄	25.16	–19.93
H ₂ O	Distilled water	–12.13	

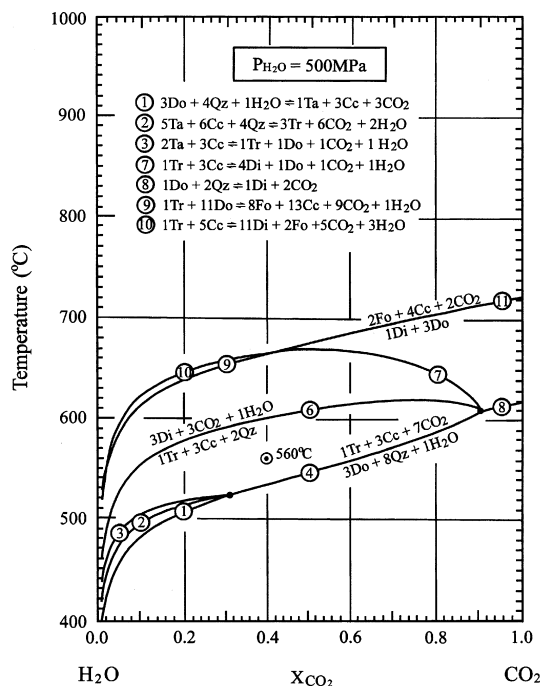


Fig. 1 Phase equilibrium diagram showing the stability field of calcite-tremolite-fluid at 500 MPa (revised after Metz 1983, and Gottschalk 1997)

Zheng et al. (1994b) for calibrating fractionation factors between calcite and tremolite in the presence of small amounts of fluid.

The weights of calcite and tremolite used in each experiment were adjusted to have the same number of oxygen atoms in each phase in order to achieve the equivalent exchange of oxygen isotopes between the two minerals. The grain size of the starting materials ranged mostly from 10 to 20 μm , with very few grains less than 10 μm in size. In the three-phase system experiments, the weight ratio of mineral to fluid (M/F) was 2.28; the mole fraction of oxygen in the mineral mixture was 0.58 and that in the fluid was 0.42. This is significantly smaller than the M/F ratios of 11.41 to 24.81 in the previous calibration experiments by Zheng et al. (1994b) in the presence of small amounts of a supercritical CO_2 - H_2O fluid.

The oxygen isotope compositions of calcite and tremolite were determined by the phosphoric acid method (McCrea 1950) and the conventional BrF_5 method (Clayton and Mayeda 1963), respectively. The oxygen isotope composition of water was determined by the CO_2 - H_2O exchange equilibrium method (Cohn and Urey 1938). CO_2 was directly frozen when opening the capsules. Isotopic ratios were measured in a MAT-252 mass spectrometer at Tuebingen. The analytical results for oxygen isotopes are reported in the $\delta^{18}\text{O}$ notation relative to the VSMOW standard. Analytical reproducibilities are typically better than $\pm 0.2\text{‰}$ for $\delta^{18}\text{O}$ in silicate, carbonate, water, and carbon dioxide. Uncertainties associated with the three-phase exchange method were estimated by Zheng et al. (1994a) and are about $\pm 0.3\text{‰}$ – 0.4‰ for the resultant fractionations between any two phases. It seems that the propagated analytical uncertainties fall within the symbol size in Figs. 2, 3, 4 and 5 if the uncertainties in individual points are plotted on these diagrams.

According to the principle of mass balance, a $\delta^{18}\text{O}$ value of 9.17‰ is calculated for the initial mixed CO_2 - H_2O fluid in the three-phase system experiments, in which the mole fraction of oxygen in CO_2 is 0.57. There is a large difference in initial $\Delta^{18}\text{O}$ (calcite-fluid), which is 6.24‰ in run series A but -1.33‰ in run series B. The initial $\Delta^{18}\text{O}$ (tremolite-fluid) is the same (2.35‰) in

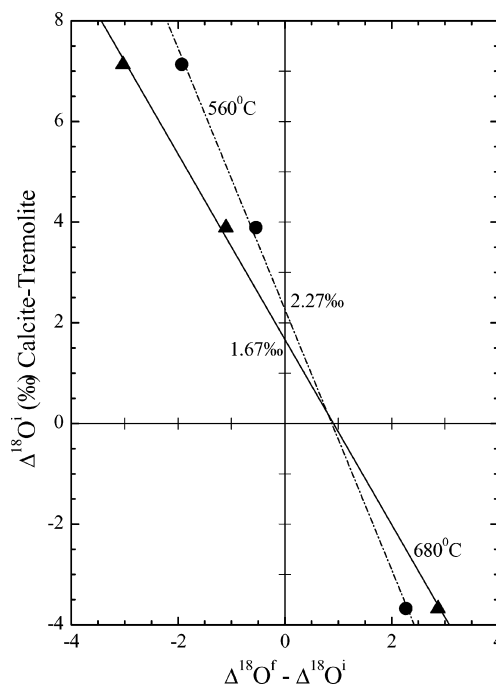


Fig. 2 Plot of experimental data for oxygen isotope exchange between calcite and tremolite in the absence of a fluid at 680 and 560 $^{\circ}\text{C}$, respectively

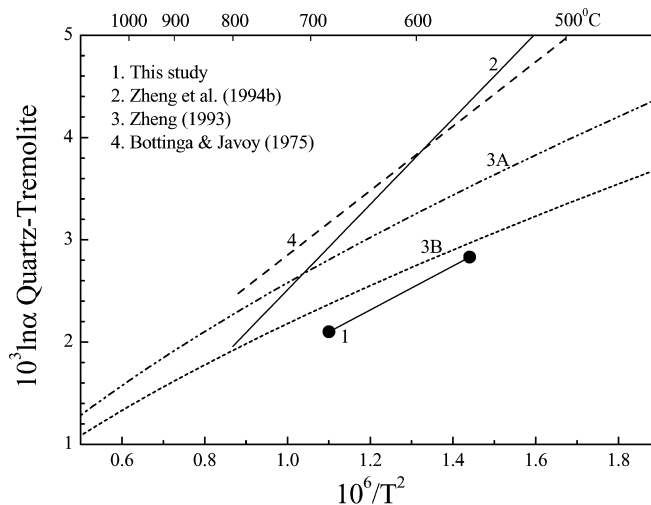


Fig. 3 Comparison of various calibrations of the quartz-tremolite equilibrium fractionation. The curve labeled 1 denotes the present experiments, 2 the previous experiments of Zheng et al. (1994b) in the presence of fluid, 3A the theoretical calculation of Zheng (1993) for tremolite by the increment method, 3B the theoretical calculation of Zheng (1993) for framework oxygen in tremolite, and 4 the empirical estimates of Bottinga and Javoy (1975) for amphibole. An $I^{18}\text{O}$ index of 0.8085 was calculated by Zheng (1993) for anhydrous tremolite, which corresponds to the following fractionation relation between quartz and framework oxygen in tremolite: $10^3 \ln \alpha = 0.42 \times 10^6/T^2 + 3.02 \times 10^3/T - 1.26$

the two run series. The $\delta^{18}\text{O}$ values of the total system in series A and B are 11.66 and 9.47‰ , respectively.

After the experiments, the gold capsules were weighed before puncturing to confirm closed-system behavior during the

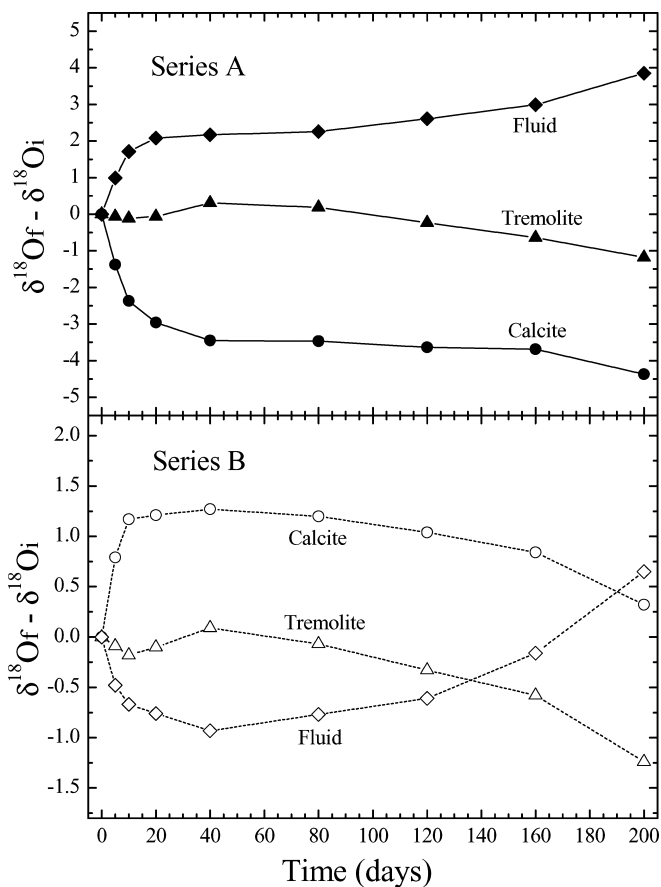


Fig. 4 Changes in the oxygen isotope composition of calcite, tremolite, and fluid as a function of exchange time. The subscripts *i* and *f* refer to initial (time=0) and final (time=*t*), respectively. Note the scale difference in the y-axis between the series A and B data

experiments. Afterwards they were pierced and dried at 110 °C before performing morphological and isotopic analyses. The mineral samples were investigated by SEM and XRD methods that show no mineral other than calcite and tremolite in the products of both fluid-present and fluid-absent runs. Dissolution-recrystallization has, however, occurred significantly, as shown by the disappearance of smaller grains and the coarsening of larger grains for the same mineral particles. Although the coarsening of tremolite also occurred in the fluid-absent runs, it is not as significant as calcite. The tremolite stability during the experiments of the two-phase system in which the only H₂O was contained in the tremolite itself was not expected, but it did occur after checking the run products. It is unclear whether the presence of tremolite in the system would buffer the H₂O fugacity at some finite value or not.

The oxygen isotope compositions of CO₂ and H₂O in the final fluids of some runs from the three-phase experiments were directly measured. The results show significant isotope exchange to different degrees between CO₂ and H₂O during quenching. Because the capsules did not leak during the experiments, the conservation of mass can be safely applied to the oxygen isotope composition of the calcite–tremolite–fluid system after the isotope exchange. For this reason, the oxygen isotope composition of the final fluids was calculated from the mass balance equation with a given confidence. Nevertheless, it is possible that the fluid at the high temperature and pressure may contain trace amounts of dissolved carbonate, bicarbonate and silicate species that may cause the isotope salt effect of dissolved minerals (Hu and Clayton 2003). Although this could affect the accuracy of calculated $\delta^{18}\text{O}$ values

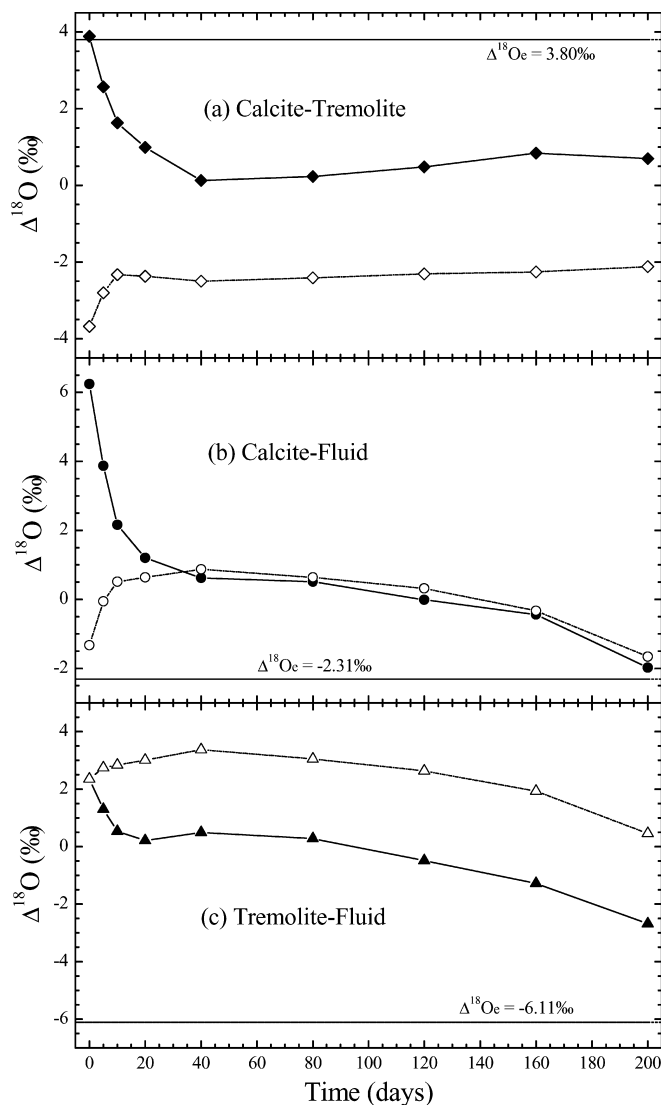


Fig. 5a–c Changes in oxygen isotope fractionations between calcite, tremolite and fluid as a function of exchange time. **a** Calcite–tremolite, **b** calcite–fluid, and **c** tremolite–fluid. *Solid circles* denote series A and *open circles* denote series B. Equilibrium fractionations are shown for different phase-pairs at 560 °C (see the text for reference)

for the final fluids, it can be reasonably assumed that the calculated $\delta^{18}\text{O}$ values provide a first approximation to the final fluid. Therefore, the calculated $\delta^{18}\text{O}$ values for the fluid are amenable to discuss the mechanistic behavior of oxygen isotope exchange from our experimental data.

Experimental results

Calcite–tremolite system

The measured $\delta^{18}\text{O}$ values of calcite and tremolite in the two sets of companion runs are presented in Table 2, along with corresponding isotope fractionations between the phases at 680 and 560 °C, respectively. Figure 2 depicts the experimental results in the extrap-

Table 2 Oxygen isotope exchange between calcite and tremolite without fluid

Temperature (°C)	Pressure (MPa)	Time (days)	$\Delta^{18}\text{O}_{\text{Cc-Tr}}^{\text{i}}$ (‰)	$\delta^{18}\text{O}_{\text{Cc}}^{\text{f}}$ (‰)	$\delta^{18}\text{O}_{\text{Tr}}^{\text{f}}$ (‰)	$\Delta^{18}\text{O}_{\text{Cc-Tr}}^{\text{f}}$ (‰)	$\Delta^{18}\text{O}^{\text{f}} - \Delta^{18}\text{O}^{\text{i}}$ (‰)	Exchange (%)	$\Delta^{18}\text{O}_{\text{Cc-Tr}}^{\text{e}}$ (‰)
560	500	20	7.13	17.61	12.38	5.20	-1.93	38.6	2.27
			3.89	15.16	11.81	3.35	-0.54		
			-3.68	9.08	10.49	-1.41	2.27		
680	1,000	7	7.13	17.44	13.34	4.10	-3.03	54.3	1.67
			3.89	15.39	12.60	2.59	-1.30		
			-3.68	9.39	10.20	-0.81	2.87		

olation plot of Northrop and Clayton (1966) according to the relation:

$$\Delta^{18}\text{O}_{\text{Cc-Tr}}^{\text{i}} = b - m(\Delta^{18}\text{O}_{\text{Cc-Tr}}^{\text{f}} - \Delta^{18}\text{O}_{\text{Cc-Tr}}^{\text{i}}) \quad (1)$$

where the superscripts i and f refer to initial and final, respectively; the subscripts Cc and Tr denote calcite and tremolite, respectively; the intercept *b* corresponds to the equilibrium fractionation between calcite and tremolite ($\Delta^{18}\text{O}_{\text{Cc-Tr}}^{\text{e}}$), and the slope *m* gives the exchange percent by 100/*m*. The present experiments yielded a $\Delta^{18}\text{O}_{\text{Cc-Tr}}^{\text{e}}$ value of 1.67‰ at 680 °C with 54.3% exchange, and 2.27‰ at 560 °C with 38.6% exchange (Table 2). The two data of extrapolated equilibrium fractionation define a straight line as expressed by the equation:

$$10^3 \ln \alpha_{\text{Cc-Tr}} = 1.77 \times 10^6 / T^2 - 0.27 \quad (2)$$

with an error estimate of about $\pm 0.2\%$. By combining the experimental quartz–calcite exchange data of Clayton et al. (1989) with the present calcite–tremolite results, a quartz–tremolite calibration is obtained as follows:

$$10^3 \ln \alpha_{\text{Qz-Tr}} = 2.15 \times 10^6 / T^2 - 0.27 \quad (3)$$

This curve is shown in Fig. 3, along with previously published calibrations by the empirical estimates of Bottinga and Javoy (1975), the theoretical calculations of Zheng (1993) for tremolite and its anhydrous equivalent, and the experimental determination of Zheng et al. (1994b) in the presence of small quantities of fluid. The differences between the various curves are large, amounting to 100–200 °C in many cases. It appears that the equilibrium fractionations extrapolated for the calcite–tremolite system are significantly lower than those by Bottinga and Javoy (1975) from natural assemblages. Similar discrepancies were also observed between experimental and empirical calibrations concerning muscovite and phlogopite (Chacko et al. 1996). When applying to mineral-pair oxygen isotope geothermometry, the experimental calibrations will yield isotopic temperatures which are unreasonably low in comparison with those predicted from the oxygen diffusion model, even under conditions of very slow cooling (Giletti 1986; Eiler et al. 1993).

It is interesting to note in Fig. 3 that the theoretical curve of Zheng (1993) for anhydrous tremolite closely matches the present experiments, whereas the

experimental curve of Zheng et al. (1994b) for whole tremolite is in agreement with the empirical data of Bottinga and Javoy (1975) for amphibole. The above discrepancy and coincidences may reflect complexities in the experimental calibrations of oxygen isotope fractionation concerning amphiboles. In other words, it is likely that the fractionations deduced by extrapolation from partial exchange between calcite and tremolite may correspond to a metastable steady-state “equilibrium” rather than a thermodynamic equilibrium. The so-called steady-state “equilibrium” refers to a kinetically controlled transition state at nonequilibrium during the processes of isotope exchange reactions, whereas the thermodynamic equilibrium corresponds to the minimum free energy for isotope exchange reactions.

Calcite–tremolite–fluid system

The series A experiments used synthetic calcite as starting material, with an initial $\Delta^{18}\text{O}$ (calcite–fluid) of 6.24‰ and a $\delta^{18}\text{O}$ value of 11.66‰ for the total system, whereas the series B experiments used natural calcite as starting material, with an initial $\Delta^{18}\text{O}$ (calcite–fluid) of -1.33‰ and a $\delta^{18}\text{O}$ value of 9.47‰ for the total system. The measured $\delta^{18}\text{O}$ values of calcite and tremolite and the calculated $\delta^{18}\text{O}$ values of fluid in all runs are presented in Table 3, along with corresponding isotope fractionations between the phases. Changes with time in the $\delta^{18}\text{O}$ values of the minerals and the fluid are illustrated in Fig. 4, where isotopic data are represented as either enrichment or depletion in ^{18}O relative to the starting materials as a function of time.

In the first 20 days, the $\delta^{18}\text{O}$ values of both calcite and fluid changed significantly and relatively homogenized with the fluid (Table 3). The calcite in series A and the fluid in series B are strongly depleted in ^{18}O , whereas the calcite in series B and the fluid in series A are considerably enriched in ^{18}O (Fig. 4). This indicates that oxygen isotope exchange between calcite and fluid is very rapid in the early stage. The SEM analysis shows that the morphological changes in calcite from the reactant to product match the characteristics of the Ostwald ripening process in which smaller, thermodynamically less stable crystals or crystal surfaces dissolve and reprecipitate as overgrowths on larger, more stable grains (Anderson and Chai 1974; Chai 1974; Matthews

Table 3 Oxygen isotope exchange experiments in the calcite–tremolite–fluid system at 560 °C and 500 MPa

Time (days)	0	5	10	20	40	80	120	160	200
Series A									
$\delta^{18}\text{O}_{\text{Cc}}$ ^a	15.41	14.03	13.04	12.45	11.96	11.94	11.77	11.72	11.04
$\delta^{18}\text{O}_{\text{Tr}}$	11.52	11.46	11.41	11.46	11.83	11.71	11.29	10.88	10.34
$\delta^{18}\text{O}_{\text{Fd}}$	9.17	10.16	10.88	11.25	11.34	11.43	11.78	12.16	13.02
$\Delta^{18}\text{O}_{\text{Cc-Tr}}$	3.89	2.57	1.63	0.99	0.13	0.23	0.48	0.84	0.70
$\Delta^{18}\text{O}_{\text{Cc-Fd}}$	6.24	3.87	2.16	1.20	0.62	0.51	-0.01	-0.44	-1.98
$\Delta^{18}\text{O}_{\text{Tr-Fd}}$	2.35	1.30	0.53	0.21	0.49	0.28	-0.49	-1.28	-2.68
Series B									
$\delta^{18}\text{O}_{\text{Cc}}$	7.84	8.63	9.01	9.05	9.11	9.04	8.88	8.68	8.16
$\delta^{18}\text{O}_{\text{Tr}}$	11.52	11.43	11.34	11.42	11.61	11.45	11.19	10.94	10.28
$\delta^{18}\text{O}_{\text{Fd}}$	9.17	8.69	8.50	8.41	8.24	8.40	8.56	9.01	9.82
$\Delta^{18}\text{O}_{\text{Cc-Tr}}$	-3.68	-2.80	-2.33	-2.37	-2.50	-2.41	-2.31	-2.26	-2.12
$\Delta^{18}\text{O}_{\text{Cc-Fd}}$	-1.33	-0.06	0.51	0.64	1.47	0.64	0.32	-0.33	-1.66
$\Delta^{18}\text{O}_{\text{Tr-Fd}}$	2.35	2.74	2.84	3.01	3.37	3.05	2.63	1.93	0.46

^aSubscript: Cc, calcite; Tr, tremolite; Fd, fluid

et al. 1983a). It appears that smaller crystals dissolve because of their higher surface energy, favoring the growth of fewer, larger crystals. The observed processes resembled dissolution accompanied by precipitation (dynamic equilibrium) in the presence of a contacting fluid phase. In contrast, the $\delta^{18}\text{O}$ values of tremolite did not change significantly with time during the first 20 days (Fig. 4). This indicates that the tremolite–fluid exchange is characterized by much slower exchange rates than those observed for calcite. The SEM analysis shows that recrystallization of tremolite is not as extensive as that for calcite. However, a decrease in $\delta^{18}\text{O}$ is observed for the tremolite with time after 40 days (Fig. 4). This may indicate an increasing rate of oxygen isotope exchange between the tremolite and the fluid in the later stage.

In the run duration between 20 and 200 days, change in the $\delta^{18}\text{O}$ values of both calcite and fluid is relatively insignificant with respect to that in the first 20 days (Fig. 4). The calcite in both series A and B is slightly depleted in ^{18}O with time, whereas the fluid in both series A and B is slightly enriched in ^{18}O . This demonstrates that oxygen isotope exchange between calcite and fluid is very slow in the later stage.

As shown in Fig. 4, the rates of change in $\delta^{18}\text{O}$ are a function of time. The $\delta^{18}\text{O}$ values of calcite, tremolite and fluid, which have changed relatively slowly from 40 to 160 days, changed somewhat remarkably from 160 to 200 days. This may point to a slight increase in exchange rate after 160 days. In the overall run duration, nevertheless, the $\delta^{18}\text{O}$ of calcite in series A is changed by about 3‰ whereas that in series B by only about 1‰. This may be due to the difference in the origin of the starting materials: calcite A is a synthetic carbonate whereas calcite B is from a natural carbonatite. It appears that the synthetic calcite has a greater rate of isotopic exchange with the fluid than does the natural calcite.

The measured fractionations between calcite and tremolite in series A show positive values of 3.89 to 0.13‰, whereas those in series B show negative values of -3.68 to -2.12‰ (Table 3). Furthermore, the fractionations in both series change slowly with time after

40 days (Fig. 5a) and appear to reach a steady state, pointing to a transition in the mechanism of isotopic exchange. Compared to the expected equilibrium fractionation of $3.80 \pm 0.3\%$ between calcite and tremolite at 560 °C (Zheng et al. 1994b), the measured fractionations between calcite and tremolite are far from equilibrium even after 200 days. It is interesting to note in Fig. 5a that the fractionation between calcite and tremolite in series A progressively deviates from the equilibrium value with time in the first 20 days, whereas that in series B changes towards the equilibrium value. Similar changes were observed in some of the previous experiments by Zheng et al. (1994b), designed to calibrate the oxygen isotope fractionation factors between calcite and tremolite in the presence of minor amounts of fluid. Nevertheless, the magnitude of the disequilibrium effect may have been much smaller in the calibration experiments because very high ratios of mineral to fluid were used by Zheng et al. (1994b).

Equilibrium oxygen isotope fractionation between calcite and CO_2 at 560 °C is -5.40% (Chacko et al. 1991), and that between CO_2 and H_2O is 7.23% (Rosenbaum 1997). In the present experiments, the mole fraction of CO_2 is 0.4 in the CO_2 – H_2O supercritical fluid. Correspondingly, the mole fraction of oxygen in H_2O is 0.43. It is thus calculated that the equilibrium oxygen isotope fractionation between calcite and fluid is $-2.31 \pm 0.3\%$ at 560 °C. As shown in Fig. 5b, the fractionations between calcite and fluid at 200 days are -1.98% in series A and -1.66% in series B. Apparently, they have approached the equilibrium value with time. The fractionations between tremolite and fluid gradually approach the equilibrium value of -6.11% , although it is still far away from the equilibrium value even after 200 days (Fig. 5c).

Discussion

As shown in Table 3, the fluid has the initial $\delta^{18}\text{O}$ value of 9.17% , which is depleted in ^{18}O relative to calcite A (15.41%) and tremolite (11.52%) but enriched in ^{18}O relative to calcite B (7.84%) in the experiments. The

initial difference in $\delta^{18}\text{O}$ between the calcite A and the fluid is 6.24‰, which is greater than the initial difference of 2.35‰ in $\delta^{18}\text{O}$ between the tremolite and the fluid. Because steeper gradients lead to higher fluxes for the same reaction of isotope exchange, it appears that the further the initial $\delta^{18}\text{O}$ value of two minerals are from the equilibrium values, the more rapid the initial change will be. This may be kinetically favorable for calcite A to more rapidly exchange oxygen isotopes with the fluid than the tremolite. On the other hand, calcite A is of synthetic origin whereas tremolite is of natural origin, which may also result in the difference of exchange rate between them. In either case, these are consistent with the observation for the first 20 days in Fig. 5b, c. The faster kinetics for the calcite–fluid exchange may simply be the larger tendency to undergo dissolution–recrystallization.

In contrast, the initial difference in $\delta^{18}\text{O}$ between the calcite B and the fluid is -1.33‰ , which is less than that of -3.68‰ between the tremolite and the fluid (Table 3). In the first 20 days, the $\delta^{18}\text{O}$ of the fluid decreased whereas the $\delta^{18}\text{O}$ of calcite B increased (Fig. 5b), pointing to isotopic exchange towards equilibrium between calcite and fluid. Since both calcite B and tremolite are of natural origin, the degree of initial disequilibrium may affect the kinetics of mineral–fluid exchange. Thus, it may be kinetically not favorable for calcite B to exchange oxygen isotopes with the fluid than the tremolite. As depicted in Fig. 5b and c, however, the observed change in $\Delta^{18}\text{O}$ between calcite B and the fluid is greater than that between the tremolite and the fluid in the first 20 days. In the experiments of both series, furthermore, the observed change in $\Delta^{18}\text{O}$ between the tremolite and the fluid is less than that between calcite and the fluid (Fig. 5b, c). As shown in Fig. 4, the changes in the oxygen isotope compositions of both calcite and fluid are much more significant than those in tremolite in the first 20 days. This suggests that the calcites have preferentially exchanged oxygen isotopes with the fluid relative to the tremolite, in either case regardless of the initial $\Delta^{18}\text{O}$ values between mineral and fluid. The SEM observations show that the extent of calcite coarsening is significantly greater than the extent of tremolite coarsening. Therefore, the rate of dissolution–recrystallization for the calcites is greater than that for the tremolite. This is consistent with the common consensus that calcite quickly achieves an equilibrium microstructure but amphibole does not. It was also observed in the previous experiments of Zheng et al. (1994b) that some of the $\Delta^{18}\text{O}_{\text{Cc-Tr}}$ values overstep the equilibrium fractionations at the experimental temperatures, and the exchange products have experienced significant dissolution–recrystallization.

In fact, the rate of oxygen transport by diffusion in fluid is much faster than that in minerals (e.g., Krynicki et al. 1979; Watson and Wark 1997). The fluid has been a medium of isotopic exchange between minerals in the three-phase system experiments. The oxygen isotope exchange between calcite and tremolite is

indirect and much slower in the experiments, whereas the oxygen isotope exchange between the minerals and the fluid is direct and much faster because the fluid is also a major exchange component of the system. The surfaces of the mineral grains may be in isotopic equilibrium with the fluid in their vicinity but not with each other. Kinetically it appears that the rate-determining step in mineral–mineral–fluid systems is the isotope exchange between the minerals and fluid. Both diffusion and dissolution–recrystallization have taken place during the exchange experiments. If the diffusion rate of oxygen in the minerals were slower than their growth rate, boundary layers would be developed around the grains of the minerals that have different oxygen isotope compositions from the bulk minerals. The efficiency of transport through such a fluid medium depends not only on diffusion rates, but also on the solubility of individual species in the fluid. The slower reaction and exchange times of the minerals imply that a steady-state gradient develops in the fluid and, thus, the intergranular fluid is not chemically and isotopically homogeneous.

The present experiments in the three-phase system demonstrate that the oxygen isotope exchange between the minerals and the fluid proceeds in two stages: first, through a surface-controlled mechanism of dissolution–recrystallization that is very fast; second, through a diffusion-controlled mechanism that is very slow. Apparently, the first stage involves mineral overgrowth by surface reactions between reactant minerals and fluid when the minerals and the fluid were out of chemical equilibrium. As shown by the XRD and SEM analyses, the new minerals have the same chemical and mineralogical compositions as the original minerals (i.e., the overgrowth of new calcite and tremolite on their unrecrystallized cores, respectively) because of the constraints from petrologic phase equilibrium (Fig. 1). Therefore, the mineral–fluid exchange in the early stage is dominated by an Ostwald ripening recrystallization mechanism, in which the recrystallized minerals develop as faceted overgrowths on original grains that have been rounded by the initial solution processes. These observations are consistent with the previous exchange experiments by Zheng et al. (1999) in the calcite–forsterite–fluid system. Because of the nature of the two stages for isotopic exchange in the three-phase systems, neither the first- nor the second-order kinetic model can provide a reasonable description of either calcite or silicates over the entire range of time studied. Furthermore, significant recrystallization of mineral precludes the possibility to retrieve oxygen diffusivity in the silicates from our exchange data.

As the mineral–fluid exchange proceeds, the Ostwald ripening would minimize the surface energies and drives the system toward chemical equilibrium at first. Even if the system has attained chemical equilibrium, coarsening could take place to reduce the interfacial energy of the system. In fact, extensive recrystallization occurred early in our experiments. This may be because the grains have

been crushed and sheared during pressurization. This is probably true of both minerals in the piston-cylinder runs, but it may be true only of calcite in the cold-seal runs. Once the dissolution-recrystallization in the system slows down or ceases, the diffusion mechanism prevails in the later stage to drive the system toward isotopic equilibrium (but not yet achieved in the present study). This observation is in agreement with the previous results from oxygen isotope exchange experiments in heterogeneous two-phase systems (e.g., Cole et al. 1983; Matthews et al. 1983b). Both the volume diffusion of oxygen within the crystal lattice of the minerals and the grain boundary diffusion of oxygen-bearing species between the minerals and the fluid are possible in the later stage. The presence of an interconnected (wetting) fluid phase in which oxygen diffusion rates are fast virtually guarantees that the surfaces of all the minerals attain isotopic equilibrium by diffusion with the fluid as fast as possible, but only the surfaces (in thickness of one monolayer or one micron?). However, it is unclear whether the equilibrium fractionations between surfaces are the same as those between mineral lattices. Furthermore, the presence of the fluid may not guarantee the achievement of isotopic equilibrium between the thickened rim of a crystal and other homogeneous crystals at different distances from it.

Implications for kinetic mechanism

The present experiments of the three-phase system suggest that calcite has a greater rate of dissolution-recrystallization than tremolite. Thus, calcite exchanges oxygen isotopes with the fluid more rapidly than tremolite in order to approach the isotopic equilibration under the experimental conditions (560 °C and 500 MPa). As a result, the outer layers (rims) of calcite more rapidly exchange oxygen isotopes with the fluid relative to those of tremolite in the course of the exchange experiments. It is expected that the isotopic analysis of the total grains of individual minerals represents the weighted average of $\delta^{18}\text{O}$ values for the mineral grains that did and did not experience dissolution-recrystallization, and thus the magnitude of change in the calcite $\delta^{18}\text{O}$ is greater than that in the tremolite $\delta^{18}\text{O}$. Nevertheless, the oxygen isotope compositions at the thickened rims of both mineral crystals may not be in thermodynamic equilibrium with each other, even though the isotopic gradient develops in the fluid rapidly because of the fast transport rates of oxygen in the fluid.

Tremolite is a hydroxyl-bearing silicate that contains oxygen on different sites. There is considerable isotope fractionation between framework and hydroxyl oxygens in amphiboles (Zheng 1993). It is theoretically possible for fluid to exchange oxygen isotopes with hydroxyl oxygen and framework oxygen at different rates. It is well known that hydroxyl oxygen can be extracted from hydroxyl-bearing silicates by thermal dehydroxylation and partial fluorination techniques (e.g., Hamza and

Epstein 1980; Bechtel and Hoernes 1990; Girard and Savin 1996). This suggests that the hydroxyl oxygen occupies weakly bonded sites relative to the framework oxygen within the silicates. Therefore, it is probable that aqueous fluid can exchange oxygen isotopes with the hydroxyl oxygen faster than with the framework oxygen. Further work is required to define what is the mobile species for oxygen isotope exchange between fluid and tremolite. If H is present in the system, this may actually be molecular H_2O . Although mobile H_2O would interact with both OH^- and O^{2-} within the tremolite lattice, different rates of isotopic exchange could be expected from the difference in bond strength. Thus, the effective rate of isotope exchange by OH^- transport would be higher than that by O^{2-} transport in any case.

When the fluid started to react with the hydroxyl-bearing silicates at the beginning of each experiment, it would preferentially exchange oxygen isotopes with the hydroxyl oxygen over the framework oxygen in the silicates. For a dissolution-recrystallization mechanism, the amount of isotopic exchange on both sites should be equal to the percent of the original solid that has been recrystallized. However, the dissolution-recrystallization mechanism can be complicated by other factors such as incomplete oxygen exchange between dissolved mineral and fluid prior to mineral recrystallization or diffusive transfer of hydroxyl oxygen into the mineral. The rate of the hydroxyl oxygen exchange can exceed that of the framework oxygen in this process. This may have complicated the processes of oxygen isotope exchange concerning hydroxyl-bearing silicates.

Matthews et al. (1983b) attempted experimentally to determine the oxygen isotope fractionation between tremolite and water at 600–700 °C and 1.34–1.78 GPa by means of the three-isotope method, but they did not obtain consistent results. They observed a decrease in $\Delta^{18}\text{O}_{\text{Tr-w}}$ with increasing temperature, from 0.03‰ at 600 °C to -0.78‰ at 700 °C with low fractional exchange ($\leq 55\%$). Using the experimental quartz–water data of Clayton et al. (1972), quartz–tremolite fractionations were calculated to be less than 2‰, which are not only significantly lower than the fractionations of 3–4‰ deduced at 600–700 °C using the empirical quartz–amphibole curve of Bottinga and Javoy (1975) as well as the experimental data of Zheng et al. (1994b), but also considerably lower than the experimental data delineated in Fig. 3 from this study. This may point to a preferential exchange between hydroxyl oxygen and water over the framework oxygen in tremolite in the hydrothermal experimental of Matthews et al. (1983b).

As shown in Fig. 3, the equilibrium fractionations deduced by extrapolation from the present two-phase calcite–tremolite exchange experiments at 560–680 °C are significantly lower than the empirical data of Bottinga and Javoy (1975) for amphibole. It was also observed by Chacko et al. (1996) for the system containing muscovite that the combined experimental calibrations of oxygen isotope fractionation between quartz and this

hydroxyl-bearing silicate are significantly lower than the empirical estimates of Bottinga and Javoy (1975) in terms of the laboratory data of O'Neil and Taylor (1969) on muscovite–water fractionation and available data on natural rock systems. Both experiments resulted in underestimates of oxygen isotope fractionations between calcite/quartz and the hydroxyl-bearing silicates. It appears that the behavior of oxygen isotope fractionation in the hydroxyl-bearing silicates is not as simple as anhydrous silicates, probably depending on kinetic processes involving oxygen exchange among different sites, diffusion species (OH and/or H₂O) and the nature of the exchange medium with which the oxygen transport proceeds (i.e., the presence or absence of a fluid and its quantity).

Sharp and Kirschner (1994) discussed the kinetic effects in oxygen isotope exchange experiments involving mineral–mineral and mineral–fluid systems, and suggested that the small fractionations measured in the direct calcite–silicate exchange experiments may be due to the slow diffusion rate of oxygen during the solid–solid reactions where significant recrystallization occurs. Hydroxyl is the major structural constituent in hydroxyl-bearing silicates, and relatively weakly bound to six or higher coordinated divalent cations. In the exchange experiments involving the hydroxyl-bearing silicates, besides the dissolution–recrystallization mechanism the diffusion of hydroxyl also plays an important role in approaching the oxygen isotope equilibration between the phases. This is because hydroxyl transport as the diffusion species is faster than H₂O molecules (Zhang et al. 1991), and thus favors continuously isotopic re-equilibration during cooling. This may be a potential cause for the underestimate of oxygen isotope fractionations between quartz and the hydroxyl-bearing silicates from the exchange experiments of the two-phase system. Because of the effect of hydroxyl on oxygen isotope fractionation in the whole mineral, it is likely that the experimental calibrations of Zheng et al. (1994b) between calcite and tremolite in the presence of small quantities of fluid have closely represented the realistic behavior of oxygen isotope exchange between natural assemblages containing amphibole.

On the other hand, the results from the experimental exchange with tremolite without fluid are very close to the calculated fractionations by Zheng (1993) for the framework oxygen in tremolite (Fig. 3). It is not unclear why there is such a coincidence. It could be due to one of the following reasons: (1) error in the calculations by means of the increment method (e.g., inappropriate estimates of hydroxyl effect on the whole mineral); (2) the partial equilibrium technique is not reliable when the amount of isotopic exchange is low; (3) kinetic effects in the direct exchange experiments due to recrystallization; and (4) complexities in experiments with exchanging oxygen on the different sites of hydroxyl-bearing silicates (e.g., variable behaviors of hydroxyl oxygen in different types of isotopic exchange experiments). It is possible that the behavior of oxygen isotope fractionation in the

hydroxyl-bearing silicates that underwent recrystallization may be different from those that did not experience recrystallization at high temperatures and high pressures.

The oxygen diffusion experiments of Farver and Giletti (1985) suggest that hydroxyl does not diffuse faster than the framework oxygen in amphiboles. In other words, the effective diffusivity of OH[−] may not be higher than that of O^{2−} in the tremolite lattice. Once dissolution–recrystallization has taken place during the exchange experiments, however, the exchange rate of oxygen isotopes on the different structural sites of amphiboles may be different from each other. As a result, OH[−] may transport faster than the molecule H₂O in hydroxyl-bearing silicates (Zhang et al. 1991). The bulk exchange is thus controlled by the atomic scale mechanism by which the hydroxyl oxygen is actually exchanged with the framework oxygen and the external material (fluid or mineral). Further experiments are required to separate the oxygens on the different sites of hydroxyl-bearing minerals, allowing independent rates of isotope exchange to be studied by the different types of exchange experiments (i.e., mineral–water, calcite–mineral and calcite–mineral–fluid).

In the later stage of the second type experiments, it can be expected that there are three kinds of oxygen isotope exchange processes by diffusion between the minerals and the fluid at the same time. The first is that between the fluid and the overgrown rims of mineral grains (recrystallized phase), which is fast and makes the minerals and the fluid approach isotopic equilibrium in a short period. It is possible that the redeposited mineral rims (overgrowths) would transiently be in, or near to, isotopic equilibrium with the fluid. Correspondingly, the δ¹⁸O value of the fluid was changing with time through isotopic exchange with the minerals. The second is that between hydroxyl and framework oxygens within the tremolite, which causes the internal isotope equilibrium of oxygen on the different structural sites. The third is that between the unrecrystallized cores and the overgrowths, which is slow and regulates the oxygen isotope gradients within the single grains of the minerals. In all of the three kinds of diffusion process, oxygen transport may be dominated by diffusion of H₂O molecules in calcite but OH in tremolite (Zhang et al. 1991; Cole and Chakraborty 2001). The OH transport as the diffusion species is faster than the H₂O diffusion and thus favors the oxygen isotope homogenization during the process of mineral–fluid interactions.

Volume diffusivity of oxygen in calcite and tremolite under hydrothermal conditions was determined experimentally, which gives an activation energy $E = 173$ kJ/mol and a pre-exponential factor $D_0 = 7 \times 10^{-9}$ m²/s for calcite (Farver 1994), and $E = 163$ kJ/mol and $D_0 = 2 \times 10^{-12}$ m²/s for tremolite (Farver and Giletti 1985). Although the activation energies for calcite and tremolite are similar, the pre-exponential factor of calcite is 3 orders of magnitude greater than that of tremolite. It turns out that the rate of oxygen isotope

exchange by volume diffusion between calcite and fluid is much faster than that between tremolite and fluid. From Fig. 5b and c, however, it appears that the magnitudes of $\Delta^{18}\text{O}$ change between calcite and fluid in the later-stage experiments are very similar to those between tremolite and fluid. This may imply in our experiments that the rates of oxygen diffusion between calcite and fluid are approximately equal to those between tremolite and fluid after both minerals experienced recrystallization in the early stage. This differs significantly from oxygen volume diffusivity from the experimental determinations in the mineral–water systems, in which the rate of oxygen volume diffusion in calcite is much faster than that in tremolite by about 3 orders of magnitude. One possible explanation for such a discrepancy is that besides volume diffusion there is also grain boundary diffusion between the recrystallized minerals and the fluid in the later-stage experiments. Grain boundary diffusion may have similar rates for both calcite and tremolite after dissolution–recrystallization.

It is well known that the distance of element diffusion across spherical grains is a function of diffusion coefficient and time, and thus generally obeys the diffusion “rule of thumb” equation (Crank 1975):

$$r \approx \sqrt{Dt} \quad (4)$$

where r is the effective diffusion radius, D is the diffusion coefficient and t is the time. According to the diffusion coefficients of oxygen in minerals under hydrothermal conditions, one can estimate the time that it takes to achieve isotopic equilibrium between minerals and fluid by the diffusion across total grains. Using a volume diffusion coefficient of $9.945 \times 10^{-20} \text{ m}^2/\text{s}$ at 560°C for calcite (Farver 1994) and the grain radii of the starting minerals (5–10 μm) as the effective diffusion radii, a time range of 2,910 days ($r=5 \mu\text{m}$) to 11,640 days ($r=10 \mu\text{m}$) is estimated to reach 100% isotope exchange (Fig. 6). From Fig. 5b it can be seen, however, that calcite has closely approached, but not yet attained, equilibrium with the fluid in our 200-day experiments.

Theoretically, Eq. (4) is for diffusion in one direction. A more appropriate equation may be for diffusion between a well-mixed fluid of limited volume and a solid of prescribed shape. Assuming that the calcite grains in our experiments can be approximated as spheres, the time required for near-complete equilibration of those grains is given by the relation (Crank 1975):

$$r \approx \frac{5}{2} \sqrt{Dt} \quad (5)$$

Using Farver’s diffusion coefficient and assuming an average grain radius of $5 \mu\text{m}$, it is calculated from Eq. (5) that about 465 days are required to equilibrate the calcite grains with the fluid in our experiments. This still disagrees with our experimental results, even if considering the fact that the effective grain radius of our powdered calcite grains may be somewhat smaller than the measured grain radius because of the presence of

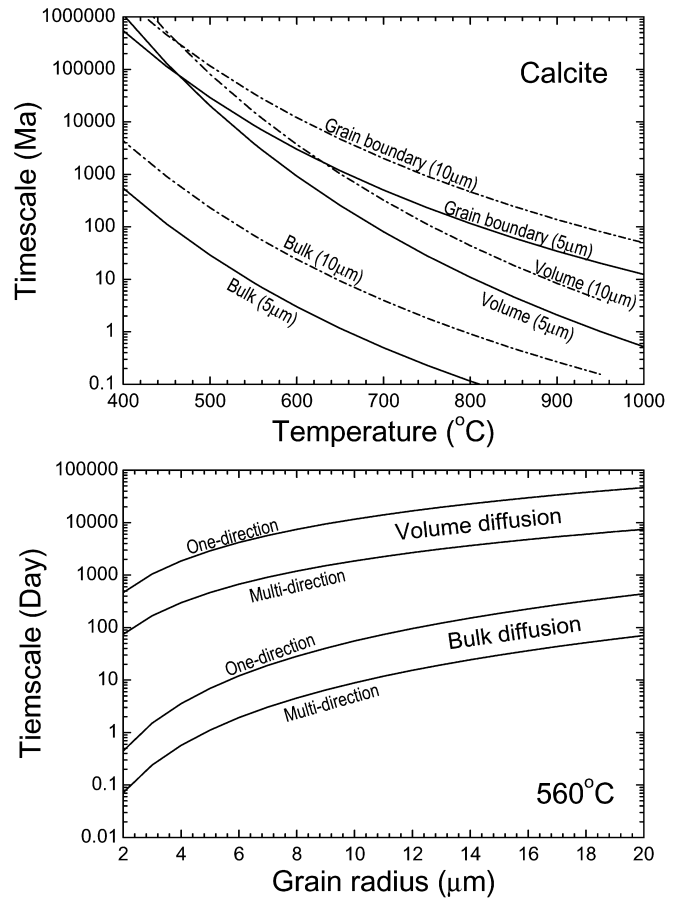


Fig. 6 Timescale for oxygen isotope re-equilibration in calcite by volume or bulk diffusion under hydrothermal conditions at different temperatures (upper diagram), and in different grain sizes (lower diagram) at 560°C . The curves represent the maximum duration by which the primary $\delta^{18}\text{O}$ value for calcite with grain radii of 5–10 μm will not be preserved due to isotopic exchange. The curves are calculated by using experimental data on volume diffusion (Farver 1994) and grain boundary diffusion (Farver and Yund 1998)

dislocation. This may indicate that the real diffusion rate of oxygen in calcite in the later-stage experiments is much greater than that expected from the experimental data of volume diffusion by Farver (1994) at the corresponding temperature. Grain boundary diffusion may also play a role accordingly because the rate of grain boundary diffusion is much faster than the rate of volume diffusion for the same mineral (e.g., Nagy and Giletti 1986; Joesten 1991; Farver and Yund 1991, 1995a, 1995b, 1998, 1999; Milke et al. 2001).

In applying the experimentally determined diffusion rates to transport through minerals, it is useful to consider the bulk (or effective) diffusivity, which represents the sum of the diffusivities of a given species through grains (volume) and along the grain boundaries. The diffusion exchange (transport) through each diffusion path is equal to the product of the diffusion rate, the concentration of diffusion species, and the fractional cross-sectional area normal to the diffusion direction for each path. In a carbonate aggregate, the concentration

of oxygen is similar in the two paths and the relationship becomes (Farver and Yund 1998):

$$D_{\text{bulk}} = D'\delta/a + D(1 - \delta/a) \quad (6)$$

where $D'\delta$ is the grain boundary diffusion coefficient, δ is the effective width of grain boundary diffusion, a is the grain diameter, and δ/a is an approximation of fractional cross-sectional area occupied by the grain boundary.

Rates of oxygen grain boundary diffusion in calcite under hydrothermal conditions were determined experimentally at 300–500 °C and 100 MPa, which give an activation energy $E = 127$ kJ/mol and a pre-exponential factor $D'_0\delta = 3.8 \times 10^{-14}$ m²/s (Farver and Yund 1998). It was estimated from the relation of $r = (4D/\delta^2)t$ that the rates of oxygen grain boundary diffusion in calcite aggregates are about 4–5 orders of magnitude greater than those of volume diffusion in calcite single crystals (Farver 1994). Using a grain boundary diffusion coefficient $D'\delta = 4.145 \times 10^{-20}$ m²/s at 560 °C for calcite (Farver and Yund 1998), and the grain radii of the starting minerals (5–10 µm) as the effective diffusion radii, 3 nm as the effective width of grain boundary diffusion, a time range of 7 days ($r = 5$ µm) to 56 days ($r = 10$ µm) is estimated to reach 100% isotope exchange by one-directional diffusion across bulk grain (Fig. 6). If the multi-directional diffusion becomes dominant, a time range of 1.9 days ($r = 5$ µm) to 8.9 days ($r = 10$ µm) is estimated to reach 100% isotope exchange. These estimates are consistent with the experimental observation in Fig. 5b that calcite has almost achieved re-equilibration with the fluid if several days more would be carried out for our experiments in the three-phase system.

Oxygen transport in intergranular regions can occur by grain boundary diffusion, ionic diffusion through a static fluid, and fluid flow. As suggested by Robie (1986), grain boundaries are considered as regions of highly disordered lattice, rather than as discrete regions separating two perfect lattices, and it is more realistic to regard water molecules as being structurally incorporated or dissolved within the grain boundaries. The transition from grain boundary diffusion to ionic diffusion in a free fluid is governed by the microstructure of the mineral grains that is influenced not only by the presence and composition of fluid but also by the thickness and interconnectedness of the fluid. The dissolution and recrystallization of calcite in the earlier stage of our experiments may be the potential process to modify the microstructure of the mineral grains and thus enhance their oxygen diffusivity in the later stage. The large differences in rate between grain boundary and volume diffusions predict already that the bulk diffusion of oxygen in minerals would be dominated by grain boundary diffusion and that oxygen transport between minerals would occur through intergranular fluids in the crust. The results from this study also indicate that the rates of oxygen isotope exchange by diffusion are much faster in the mineral near-surface than in the normal lattice, due to different mechanisms of diffusion.

Both the chemical and isotopic aspects of fluid transport in the crust are strongly determined by the behavior and quantity of the fluid phase in host rocks. The actual behavior and quantity of fluids in localized regions of the crust is not directly observable, so our conceptualizations of fluid nature are often poorly constrained. The previous experimental studies show that the uniform dispersal of a small amount of fluid on the scale of mineral grains can efficiently speed up isotopic exchange toward thermodynamic equilibrium by the mechanism of surface reactions between the fluid and the individual mineral grains (Zheng et al. 1994a, 1994b). On the other hand, the present experiments demonstrate that localization of fluids on a scale significantly larger than the mineral grains tends to minimize the isotopic heterogeneity between minerals by more effective surface reactions to drive the system toward chemical equilibrium at first, and then approach isotopic equilibrium by grain boundary diffusion between the fluid and the mineral grains.

Conclusions

The systematics of oxygen isotope exchange between calcite and tremolite has been experimentally investigated not only in the two-mineral system without fluid but also in the three-phase system containing a large amount of CO₂-H₂O supercritical fluid within the T - P - X_{CO_2} stability field of the minerals. The extrapolated equilibrium fractionations between calcite and tremolite from the two-phase system experiments are significantly lower than the empirical estimates of Bottinga and Javoy (1975) for amphibole, and the experimental determinations of Zheng et al. (1994b) in the presence of small quantities of fluid, but closely match the calculated fractionations by Zheng (1993) using the increment method for framework oxygen in tremolite. It appears that there are considerable complexities in experiments exchanging oxygen on the different sites of amphiboles in different types of exchange experiments (i.e., mineral-water, calcite-mineral and calcite-mineral-fluid). The small fractionations measured in the direct calcite-tremolite exchange experiments may be due to the different rates of oxygen isotope exchange between hydroxyl oxygen, framework oxygen and calcite during the solid-solid reactions where significant recrystallization occurs. It is possible that the behavior of oxygen isotope fractionation in the hydroxyl-bearing silicates that underwent recrystallization may be different from those that did not experience recrystallization at high temperatures and high pressures.

An important feature of the three-phase system experimental data is that the oxygen isotope compositions of calcite and tremolite were relatively homogenized with the fluid in the first 20 days, and the fractionations change rapidly for both mineral-mineral and mineral-fluid systems. Afterwards the fractionations between calcite and tremolite change very slowly

and seem in a steady state, whereas the fractionations between the minerals and the fluid change slowly towards equilibrium. As a result, the materials do not monotonically approach the equilibrium fractionations like isotopic exchange in simple two-phase systems. Like the previous experiments of Zheng et al. (1999) for the calcite–forsterite–fluid system, the minerals experienced surface-controlled isotopic exchange through dissolution–recrystallization in the early stage but diffusion-controlled isotopic exchange through transport of oxygen-bearing species in the later stage. Oxygen isotope redistribution during the process of the mineral–fluid interactions is initially controlled primarily by the Ostwald ripening process, and then becomes diffusion-controlled afterwards when the system has attained chemical equilibrium. The change in $\delta^{18}\text{O}$ values of both calcite and fluid is very significant during the dissolution–recrystallization, but becomes relatively insignificant during the diffusion. The rates of oxygen isotope exchange through dissolution–recrystallization are much faster than those through diffusion, in agreement with the exchange experiments for mineral–water systems.

Calcite has a greater rate of dissolution–recrystallization than tremolite in the presence of a large amount of fluid, which was initially far from chemical equilibrium with the starting minerals. As a result, calcite can preferentially exchange oxygen isotopes with fluid relative to tremolite. Furthermore, synthetic calcite shows a greater rate of isotopic exchange with fluid than natural calcite. Once diffusion becomes a dominant mechanism for further isotope exchange in the three-phase system, the rate of oxygen diffusion in calcite is equal to or slightly greater than that in tremolite. This differs significantly from oxygen volume diffusivity determined by hydrothermal experiments in two-phase systems, in which oxygen volume diffusion in calcite exceeds that in tremolite by about 3 orders of magnitude. Grain boundary diffusion prevails for the mineral grains in the later stage.

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