

Oxygen isotope disequilibrium between calcite and forsterite in the presence of a large amount of fluid

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Oxygen isotope studies of natural systems have revealed the presence of mineral assemblages clearly out of isotopic equilibrium. Fluid-rock interactions have been recognized to play important roles in this aspect. Kinetic experiments of isotopic exchange were normally conducted in two-phase systems (i.e. between a mineral and a fluid), which are rarely responsible for natural occurrences in poly-mineral assemblages. Cole *et al.* (1992) carried out experiments of oxygen isotope exchange between granitic minerals and water under hydrothermal conditions. However, there are alteration minerals in their reaction products. We report here hydrothermal experiments of oxygen isotope exchange between calcite and forsterite in the presence of a supercritical fluid without formation of new mineral phases.

Methods

The experiments were conducted in standard cold-seal pressure vessels at 680 and 5 kb for 10, 20, 40 and 80 days, respectively. The fluid was a mixture of H₂O and CO₂, with the mole fraction of CO₂ being 0.1. The experiments were performed in the T-P-X_{CO₂} stability field of the calcite-forsterite assemblage. The experimental methodology was closely following previous runs for calibrating fractionation factors (Zheng *et al.*, 1994).

The weight ratio of mineral to fluid in the starting mixture is 1.46; the mole fraction of oxygen in the mineral is 0.44 and that in the fluid is 0.56. The weights of calcite and forsterite used in each experiment were chosen to contain the same number of oxygen atoms. The grain size of the starting materials was mostly in the 10 to 20 μ m. After the experiments the mineral samples have been tested by SEM and XRD methods which showed that no new phases were present. Dissolution and recrystallization have taken place significantly,

which may be the major mechanism of the isotopic exchange.

The oxygen isotope compositions of calcite and forsterite have been measured, respectively, by the phosphoric acid method and the laserprobe technique. The $\delta^{18}\text{O}$ values of two starting calcites are 17.93 and 15.41‰, respectively; the $\delta^{18}\text{O}$ value of a starting forsterite is 10.60‰. The $\delta^{18}\text{O}$ value of the initial fluid is -5.34‰. The $\delta^{18}\text{O}$ values of the total system in the run series A and B are 3.29 and 2.73‰, respectively. The oxygen isotope composition of final fluids were calculated according to the principle of mass balance.

Results

Table 1 lists the oxygen isotope compositions of calcite, forsterite and fluid in the different time-lengths of isotopic exchange and corresponding fractionations. Figure 1 depicts variations in the

TABLE 1

Time (d)	0	10	20	40	80
Series A					
$\delta^{18}\text{O}_{\text{Cc}}$	17.93	3.32	3.53	3.83	4.01
$\delta^{18}\text{O}_{\text{Fo}}$	10.60	2.90	3.51	4.71	5.41
$\delta^{18}\text{O}_{\text{Fd}}$	-5.34	3.43	3.10	2.52	2.17
$\Delta^{18}\text{O}_{\text{Cc-Fo}}$	7.33	0.42	0.02	-0.88	-1.40
$\Delta^{18}\text{O}_{\text{Cc-Fd}}$	23.27	-0.11	0.43	1.31	1.84
Series B					
$\delta^{18}\text{O}_{\text{Cc}}$	15.41	1.35	1.63	3.03	3.17
$\delta^{18}\text{O}_{\text{Fo}}$	10.60	1.08	1.73	3.83	5.79
$\delta^{18}\text{O}_{\text{Fd}}$	-5.34	3.92	3.56	2.18	1.36
$\Delta^{18}\text{O}_{\text{Cc-Fo}}$	4.81	0.27	-0.10	-0.80	-2.62
$\Delta^{18}\text{O}_{\text{Cc-Fd}}$	20.75	-2.57	-1.93	0.85	1.81

Subscripts: Cc-calcite, Fo-forsterite, and Fd-fluid

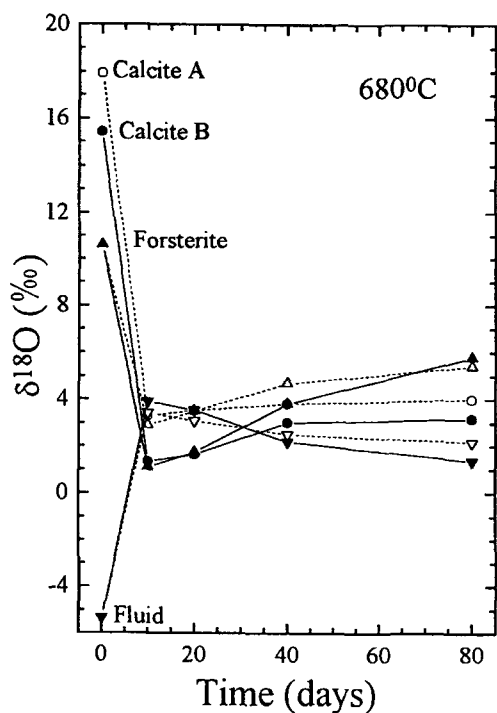


FIG. 1.

$\delta^{18}\text{O}$ values of the phases with time. Apparently, the oxygen isotope compositions of calcite and forsterite are relatively homogenized with the fluid at the first 20 days. Afterwards forsterite is progressively enriched in ^{18}O relative to calcite.

With increasing exchange time the oxygen isotope fractionations between calcite and forsterite decrease progressively from 7.33 to -1.40‰ in series A and from 4.81 to -2.62‰ in series B, respectively. It appears that the measured fractionations passed the equilibrium value of $3.67 \pm 0.2\text{‰}$ at 680°C (Chiba *et al.*, 1989) after isotopic exchange in few days and went far away from equilibrium. They have not come back to the equilibrium fractionation even after 80 days. The $\delta^{18}\text{O}$ values of the final fluids are

progressively depleted in ^{18}O with time relative to both calcite and forsterite. The fractionations between the fluid and the calcites are also at disequilibrium with respect to the equilibrium value of -0.58‰ (Chacko *et al.*, 1991).

The results from the present experiments suggest that: (1) forsterite can be enriched in ^{18}O relative to calcite due to the presence of a large amount of fluid. This is different from not only those in the presence of a trace amount of fluid but also those in the absence of fluid; (2) fractionation behaviours between minerals and fluid in a three-phase system are different from those in the two-phase systems of mineral-fluid; (3) oxygen isotope equilibration was not able to be achieved between calcite and forsterite by the pure isotopic exchange of low free-energy changes, even if there is a significant amount of fluid as the exchange medium. These provide an insight into the kinetics of isotopic exchange between minerals in the presence of fluid and the nature of fluid/rock interaction.

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