Hydrogen isotope disequilibrium among hydrous minerals in eclogites from the Dabie Mountains and the Sulu terrane

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Both equilibrium and disequilibrium of oxygen isotopes have been observed among minerals in ultrahigh pressure (UHP) eclogites from the Dabie Mountains and the Sulu terrane in East China. Fluid-rock interactions have been assumed to occur before and after the UHP metamorphism. However, it is unclear how hydrogen isotopes behave in eclogites during the fluid-rock interactions. This study reports the hydrogen isotope disequilibrium in hydrous minerals from a number of eclogites in the Dabie Mountains and the Sulu terrane.

Methods

Eclogite samples were collected from Shuanghe in the eastern part of the Dabie Mountains and Donghai in the western part of the Sulu terrane. The two areas are separated from each other by the Tanlu Fault for over 500 km. Unusually low $\delta^{18}O$ values of -8 to $-10‰$ have been reported for mineral separates from eclogites at Qinglongshan within the Donghai district (Yui et al., 1995; Zheng et al., 1998).

All mineral separates were obtained by hand-picking under a binocular microscope. Clean and pure mineral separates were essential to obtain credible isotope analyses. Hydrogen from hydroxyl-bearing silicates was liberated by reaction with hot zinc metal to produce H_2 for isotopic analysis.

Results

The δD values of hydrous minerals from the eclogites fall in the limited ranges of -104 to $-73‰$, -93 to $-81‰$ and -66 to $-49‰$ for phengite, amphibole and zoisite, respectively. As shown in Fig. 1, hydrogen isotope fractionations between zoisite and phengite vary regularly with variations in the δD values of the individual minerals.

If the isotope fractionation behaviour of hydrogen in phengite is assumed to be closer to muscovite than biotite, the sequence of D-enrichment in the coexisting phengite, amphibole and zoisite from both Donghai and Shuanghe is just reversed with respect to that predicted from experimental studies for equilibrium fractionation at temperatures above 500°C (muscovite > amphibole > zoisite). Both retrograde metamorphism and pressure effect are likely responsible for such disequilibrium fractionations.

Experimental studies of hydrogen isotope exchange kinetics under hydrothermal conditions of 2 to 4 kbar suggest that the rate of hydrogen diffusion in the hydrous minerals is muscovite < amphibole < zoisite (Graham, 1981). This implies that closure temperatures for cessation of hydrogen isotope exchange would follow the sequence of muscovite (phengite) > amphibole > zoisite. Since the hydrous minerals are the principal internal reservoir for hydrogen under conditions of the UHP metamorphism, isotopic reequilibration among them was unavoidable.

Oxygen isotope disequilibrium between garnet and the other minerals such as omphacite, phengite and/or quartz has been observed in some of the eclogite
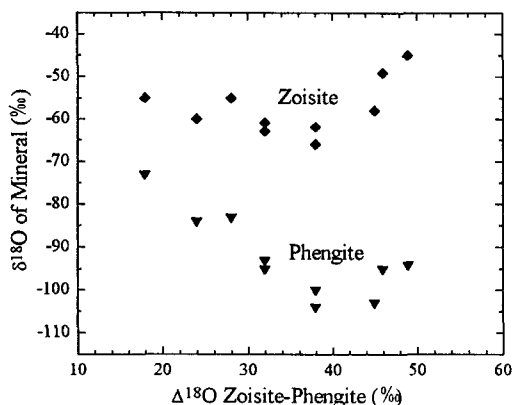

FIG. 1.

samples from the Dabie and Sulu terranes. This has been ascribed to retrograde reactions such as the sympletitic replacement after omphacite and/garnet and the formation of edenitic/pargasitic amphibole during the eclogite exhumation. The reported P-T conditions for the retrograde metamorphism of the eclogites cover a wide range, P = 6 to >20 kbar and T = 470 to >680°C.

At the temperatures of the eclogite-facies metamorphism, hydrogen isotope fractionations between muscovite (phengite) and water are smaller than −10‰ (Suzuoki and Epstein, 1976). Hence, the δD values of the white-mica minerals would resemble those of water with which the rocks equilibrated at the high temperatures. This indicates the involvement of meteoric water in the formation of the eclogites. The unusual δD values as low as −104 to −100‰ for phengite from Donghai eclogites imply that the ancient meteoric water could have lower δD values than modern meteoric water in East China. In this regard, hydrogen isotope exchange between the fluid and the hydroxyl phases could have occurred near the surface prior to subduction.

With respect to the reversed hydrogen isotope fractionation between phenigite and zoisite one logical explanation is that the hydrous minerals acquired their low δD values by interaction with meteoric water before plate subduction and eclogitization, and hydrogen isotope equilibration was achieved during the UHP metamorphism, but the equilibrium fractionation has been disturbed by the differential exchange of hydrogen isotopes between phengite, amphibole, zoisite and fluid due to retrograde alteration during exhumation. Because of the difference in the rate of hydrogen diffusion, phengite has probably preserved its primary hydrogen isotope composition to the greatest degree, whereas zoisite has preserved its primary hydrogen isotope composition to the least degree.

Since the retrograde fluid-rock interaction subsequent to the UHP metamorphism can be taken place under very high presssures, pressure effect on hydrogen isotope fractionation factors between minerals and water may be not negligible (Driesner, 1997). Hydrothermal exchange experiments obtained that hydrogen isotope fractionation factors between epidote and water (ΔD_{Ep-W}) are about −35‰ at 2 to 4 kbar and >400°C (Graham et al., 1980). If the factors would be taken to calculate the hydrogen isotope composition of the retrograde fluid in isotopic equilibrium with epidote from the eclogites in question, the δD values obtained are −33 to −23‰ which correspond to an external fluid like paleoseawater or formation water.

Taking into account the calculations of Driesner (1997), However, it can be expected that the ΔD_{Ep-W} values would increase significantly at higher pressures (e.g. >20 kbar). As a result, the δD values of the retrograde fluid can be close to, or even greater than those of the epidote from the eclogites due to the pressure effect. Thus the hydrogen isotope data indicate an internally buffered fluid for the retrograde fluid-rock interaction.

Acknowledgements

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