Water of garnet in Dabie UHP eclogite: implication for fluid action in continental subduction zone

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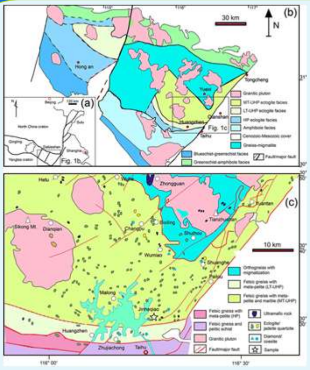


Fig. 1. Geological sketch map of the Dabie orogen showing major lithotectonic units and the sample location

Introduction

Understanding water transport and its effect in the subduction zone is crucial for volatile cycling of the Earth, geodynamics of the subduction zone and the habitability of the Earth. Due to decomposition of hydrous minerals, water is incorporated in nominally anhydrous minerals during subduction. As one of the most important nominally anhydrous mineral in eclogitized continental crust, garnet from UHP eclogite plays a key role in water cycle from crust to upper mantle. We carried out a combined study of major element, trace element and water content in garnet as well as oxygen isotope analyses of rock-forming minerals for eclogites from the Dabie orogen (Fig. 1). The results were used to provide constraints on the role of garnet in the water transport in the continental subduction zone.

Samples

Four fresh massive eclogite samples collected from the Jinheqiao area in the Dabie orogenic belt are used in this study. X-ray fluorescence mapping are used to calculate mineral proportion. The representative mineral assemblages are garnet (25-33 vol.%) and omphacite (50-55 vol.%) with varying amounts of quartz (2-6 vol.%), phengite (0-7 vol.%), amphibole (4-7 vol.%), zoisite (1-3 vol.%) (Fig. 2). Accessory minerals containing kyanite, rutile, apatite, titanite and zircon are all lower than 2 vol.%.

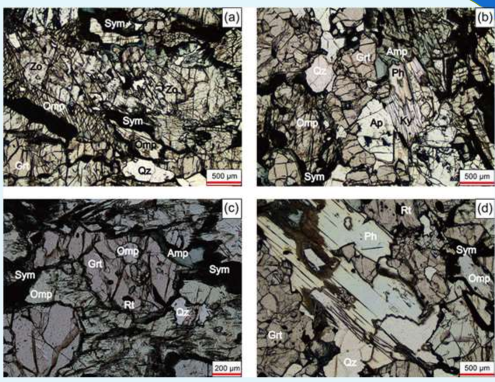


Fig. 2. Photomicrographs of the Jinheqiao eclogite

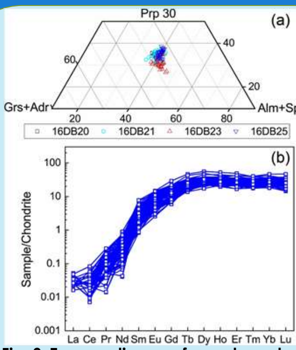


Fig. 3. Ternary diagram for endmember contents and chondrite-normalized REE patterns for garnet

Mineral chemistry of garnet

Garnet major elements show large variations among different grains in the same sample and different samples. The concentrations of almandine, grossular, pyrope and spessartine are from 34.7 to 51.3 mol%, 20.1 to 31.9 mol%, 18.7 to 38.5 mol%, and 0.59 to 1.78 mol%, respectively. In contrast, individual garnet grain shows relatively homogeneous or very weak zoning in major element compositions. All the garnet grains show homogeneous rare earth element compositions with flat HREE patterns and no Eu anomalies.

Characteristics of IR spectra and water content of garnet

The absorption bands of garnet at 3000-3800 cm^{-1} can be divided into five groups: 3360-3450 cm cm^{-1} (Group M), 3500-3530 cm cm^{-1} (Group 1), 3540-3580 cm cm^{-1} (Group 2), 3580-3630 cm^{-1} (Group 3), and 3635-3665 cm^{-1} (Group 4). The broad infrared absorption band of Group M is ascribed to molecular water in the form of submicroscopic fluid inclusion, whereas the other bands are ascribed to structural hydroxyl. All the absorption spectra can also be divided into type 1 without molecular water and type 2 with molecular water. Most of type 1 garnet points have structural water lower than 40 ppm. Type 2 garnet points have structural water of 11-1891 ppm with an average of 387 ppm, and molecular water of 3-1552 ppm with an average of 315 ppm.

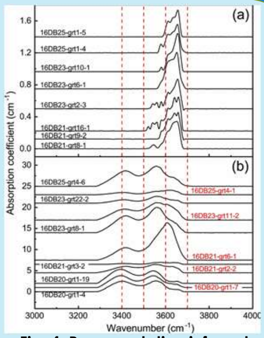


Fig. 4. Representative infrared absorption spectra of garnet

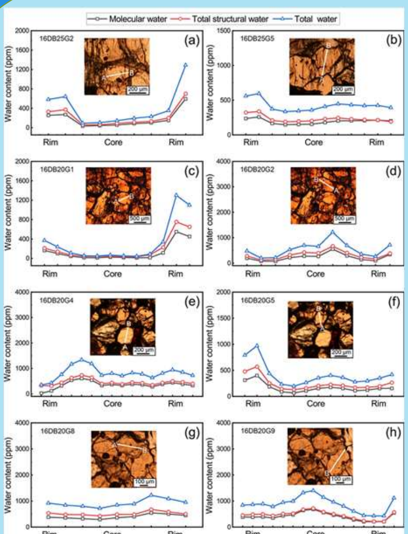


Fig. 5. Representative water profiles of garnet

Water profile

Different water distributions were observed in garnet grains from core to rim. Garnet with total water content lower than 400-800 ppm in the core shows an increase in water content from core to rim, whereas that with total water content higher than 1000 ppm in the core shows a decrease in water content from core to rim. In addition, the outmost rim of the former one exhibits an decrease when total water content is higher than 400 ppm. While total water content of the latter one is lower than 400-800 ppm, reverse trend can be observed . It is noted that reverse water profiles of garnet are common among the adjacent garnet grains.

Source of molecular water

The genesis and source of molecular water in garnet is critical for water storage capacity of garnet. The increase of structural hydroxyl contents from core to rim in some garnet grains, which were partly adjacent to symplectites, probably indicates addition of molecular water during retrogression. However, water profile with much higher water content in the core than the rim is unlikely caused by external water during exhumation, instead is generally considered as the result of water diffusion during exhumation. Garnet inclusion in omphacite that can escape from affect of external fluid, still contain molecular water (Fig. 6).

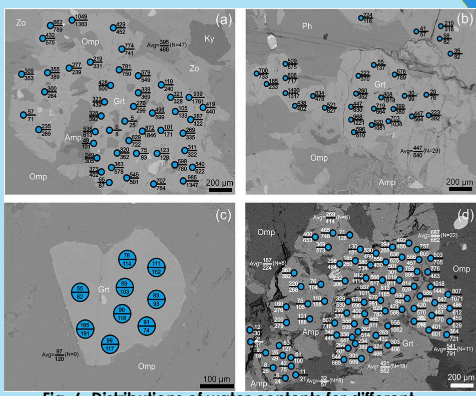
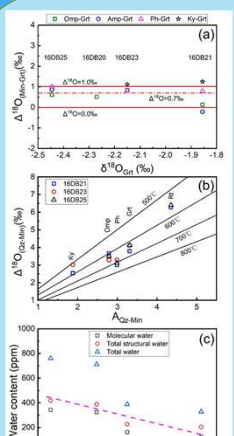


Fig. 6. Distributions of water contents for different occurrences of garnet

Garnet in the eclogite lack of fluid action also contain molecular water (Wang et al., 2018). The enhancement of hydroxyl content from molecular water during exhumation requires that peak garnet is water-unsaturated. However, garnet in the Shuanghe eclogite contain hydroxyl up to 2500 ppm (Liu et al., 2016), indicating that peak garnet can be saturated in water. Molecular water has also been observed in synthetic garnet and as primary fluid inclusion in natural peak garnet. All these observations indicate that the molecular water is internal origin of garnet.



Factor controlling water content of garnet in subduction zone

Garnets in the Jinheqiao eclogites have $\delta^{18}O$ values lower than normal mantle, indicating their protoliths experienced high-T meteoric hydrothermal alteration before subduction. The oxygen isotope equilibrium between garnet and omphacite implies that garnet $\delta^{18}O$ values can reflect the extents of hydrothermal alteration of protolith. In this regard, lower $\delta^{18}O$ value of garnet indicates higher extent of hydrothermal alteration and thus higher protolith water content. Average garnet water content exhibits a well negative correlation with garnet $\delta^{18}O$ value (Fig. 7), indicating that garnet water content was controlled by the protolith water content of its host rock, which dictates the fluid availability during subduction zone metamorphism. There are contrast correlations between garnet water content and the modal contents of phengite and zoisite, indicating the effect of fluid availability on garnet water content during garnet growth.

Fig. 7. Oxygen isotope fractionations among minerals and the relationship between average water content and $\delta^{18}O$ values of garnet for the Jinheqiao eclogite

Water transport in the continental subduction zone

Structural hydroxyl was heterogeneously incorporated into garnet during its formation, rare molecular water can also be present in this garnet. With the increase of pressure and temperature, hydrous minerals continuously breakdown and water solubility of garnet increases, resulting in the gradual enhancement of garnet water content until peak metamorphism. During this prograde metamorphism, molecular water within garnet and from decomposition of hydrous minerals was both transformed into hydroxyl in garnet. However, the heterogeneity of garnet water content and its dependence on protolith water content indicate that not all garnet grains reach water saturation at peak condition. This incomplete transformation from molecular water to structural water suggests channelized fluid flow and quick subduction of the subducting slab. Hydroxyl in both garnet and hydrous minerals stable at peak metamorphic condition was partly transformed into molecular water, which would further be redistributed into garnet or retrograde minerals.

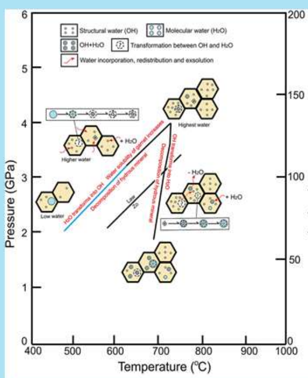


Fig. 8. Schematic cartoon showing variation of water in garnet during subduction and exhumation of the deeply subducted slab