

Mineral oxygen isotope and hydroxyl content changes in ultrahigh-pressure eclogite–gneiss contacts from Chinese Continental Scientific Drilling Project cores

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ABSTRACT A combined study of mineral O isotopes and hydroxyl contents was carried out for the contacts between ultrahigh-pressure eclogite and gneiss from main hole of the Chinese Continental Scientific Drilling Project in the Sulu orogen. While there is a large $\delta^{18}\text{O}$ variation from -8.3 to 7.3‰ for all minerals, different styles of mineral-pair fractionation occur at the boundaries of different lithologies. Both equilibrium and disequilibrium O isotope fractionations are observed between quartz and the other minerals, with reversed fractionations between omphacite and garnet in some samples of eclogite. This suggests that both eclogite and gneiss acquired their negative $\delta^{18}\text{O}$ values by meteoric-hydrothermal alteration of their protoliths at high temperatures before subduction, and that fluid-assisted O isotope exchange did take place across the boundary of different lithologies at local scales during amphibolite-facies retrogression. Fourier Transform Infrared Spectroscopy analysis yielded H_2O concentrations of 50 to 1144 p.p.m. (by weight) for garnet and 139 to 751 p.p.m. for omphacite. The state of equilibrium or disequilibrium O isotope fractionations between omphacite and garnet are correlated with variations in their water content at local scales, indicating that the internally derived fluid plays a critical role in retrograde metamorphism during exhumation. The retrograde metamorphism results in mineral reactions and O isotope disequilibria between some of the minerals, but the fluid for retrogression was derived from the decompression exsolution of structural hydroxyl and thus internally buffered in the O isotope composition. A quantitative estimate suggests that a hand specimen ($3 \times 6 \times 9$ cm) of eclogite composed of 70% garnet and 30% omphacite can release 0.316 g water by the decompression exsolution of structural hydroxyl, which can form 14.4 g amphibole during exhumation. This provides sufficient amounts of water for the amphibolite-facies retrogression.

Key words: Chinese Continental Scientific Drilling; eclogite; fluid; gneiss; hydroxyl; O isotope.

INTRODUCTION

The Dabie-Sulu orogenic belt in east-central China is well known for the largest exposure of Triassic ultrahigh-pressure (UHP) metamorphic rocks in the world (e.g. Cong, 1996; Liou *et al.*, 1996; Carswell & Compagnoni, 2003; Chopin, 2003; Rumble *et al.*, 2003; Zheng *et al.*, 2003). Discovery of coesite, diamond and extreme ^{18}O -depletion in eclogites from this exciting region has contributed much to our understanding of continental subduction to mantle depths and its subsequent exhumation (e.g. Okay *et al.*, 1989; Xu *et al.*, 1992; Yui *et al.*, 1995; Zheng *et al.*, 1996). Since the discovery of a negative O isotope anomaly in UHP eclogite at Qinglongshan in the Sulu orogen (Yui *et al.*, 1995; Zheng *et al.*, 1996), a large number of studies has been made on stable isotope geochemistry of UHP metamorphic rocks, which has been successfully used to characterize chemical geodynamics and fluid regime during con-

tinental subduction and exhumation (Zheng *et al.*, 2003, and references therein). The anomalously low $\delta^{18}\text{O}$ values of -11 to -2‰ in the UHP eclogite and gneiss indicate both intensive and extensive O isotope exchange of meteoric water with their protoliths before Triassic UHP metamorphism (Yui *et al.*, 1995, 1997; Zheng *et al.*, 1996, 1998, 1999, 2003, 2004; Baker *et al.*, 1997; Rumble & Yui, 1998; Fu *et al.*, 1999; Rumble *et al.*, 2000, 2002; Xiao *et al.*, 2002). Very limited fluid mobility is demonstrated to occur during UHP metamorphism by the Triassic subduction of continental crust to mantle depths (Rumble *et al.*, 2000; Fu *et al.*, 2001; Zheng *et al.*, 2003). On the basis of a comprehensive study on O isotopes in UHP metamorphic minerals from the Dabie-Sulu orogenic belt, Zheng *et al.* (2003) demonstrated that continent–continent collision is characterized by fast subduction and fast exhumation of cold slabs with short-lived residence for UHP metamorphism at mantle depths. Stable isotope studies are thus a

powerful tool for deciphering the geochemical processes involving UHP metamorphism of crustal rocks at mantle depths.

With respect to preservation of the UHP metamorphic minerals during exhumation, fluid–rock interactions appear to have played a critical role. Compared with the subduction of oceanic crust, continental subduction zones are characterized by the absence of syn-subduction island-arc magmatism, indicating a relative lack of metamorphic fluid during subduction (Liou *et al.*, 1997; Ernst *et al.*, 1998). During exhumation, nevertheless, significant amounts of aqueous fluid could be liberated from the decomposition of hydrous minerals, the decrepitation of primary fluid inclusions, and the exsolution of structural hydroxyl due to a pressure decrease, resulting in amphibolite-facies retrogression, formation of HP quartz veins within eclogites and syn-exhumation magmatism (Zheng *et al.*, 2003). Although some studies have been devoted to fluid mobility in HP to UHP metamorphic rocks that formed during subduction of continental crust (Rumble, 1998; Philippot & Rumble, 2000; Rumble *et al.*, 2003; Zheng *et al.*, 2003), knowledge concerning the origin of retrograde fluid is still scarce (Yardley *et al.*, 2000; Miller *et al.*, 2002). In addition to mineralogy, fluid inclusions and stable isotopes, measurements of structural hydroxyl in nominally anhydrous minerals have proved to be an effective way to study the availability of metamorphic fluid during plate subduction and exhumation (e.g. Katayama & Nakashima, 2003; Su *et al.*, 2004; Xia *et al.*, 2005; Katayama *et al.*, 2006).

In order to reconstruct the formation and exhumation mechanisms of UHP metamorphic terranes, the Chinese Continental Scientific Drilling (CCSD) Project has been carried out in the Sulu orogen (Xu *et al.*, 1998; Xu, 2004). Eclogite, gneiss, amphibolite (retro-

graded from eclogite), ultramafic rocks, and minor schist and quartzite have been recovered from drill cores. These core samples have proved valuable for the purpose of revealing the fluid behaviour in a vertical sequence of an UHP slab. Thus, continuous drill core samples with contrasting lithologies from the CCSD project provide a unique opportunity to study the petrographic transition and fluid metasomatism between mafic and felsic rocks during UHP metamorphism and its retrogression. Such transitions are not well exposed in the Dabie–Sulu orogenic belt and could provide crucial information on fluid availability in subducted crust. Oxygen isotope and fluid inclusion distributions through vertical sections from 100 to 3000 m for CCSD main hole (MH) have been investigated by Xiao *et al.* (2006). Our paper presents a combined study of the O isotope composition of mineral separates and the hydroxyl concentration of nominally anhydrous minerals at the contact between UHP eclogite and gneiss of two core segments from CCSD-MH. The results are used not only to test whether the unusually low $\delta^{18}\text{O}$ values for the UHP metamorphic rocks at great depths are inherited from their protolith, but also to study the origin and behaviour of metamorphic fluid during exhumation.

GEOLOGICAL SETTING AND SAMPLES

The Dabie–Sulu orogenic belt was formed by Triassic subduction of the South China Block beneath the North China Block (e.g. Cong, 1996; Liou *et al.*, 1996; Zheng *et al.*, 2005). It is truncated at its eastern end by the Tanlu fault, which offsets the UHP Dabie complex by ~500 km northward to the Shandong Peninsular where it is known as the Sulu orogen (Fig. 1). According to field occurrence and country-rock association, three types of eclogite have generally been

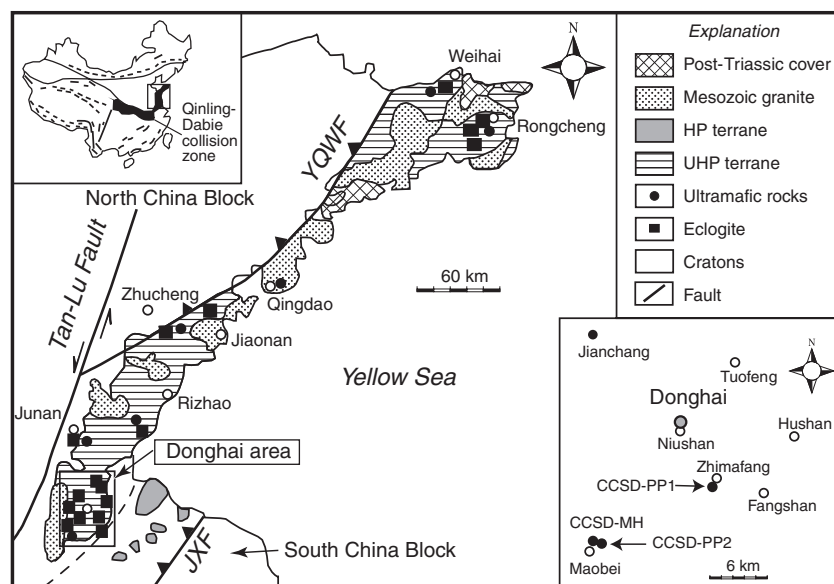


Fig. 1. Geological sketch map of the Sulu orogen and the Donghai area, showing major lithotectonic units and the location of outcrops and pre-pilot drillholes CCSD-PP1, CCSD-PP2 and the main hole CCSD (modified after Liu *et al.*, 2001). YQWF, Yantai-Qingdao-Wulian Fault; JXF, Jiashan-Xiangshui Fault.

categorized in this orogenic belt (Zheng *et al.*, 2003 and references therein): (1) G-type, gneiss-hosted enclaves or layers; (2) M-type, interlayers with or enclaves within marble or metasilicates of sedimentary protolith (including jadeite quartzite); (3) P-type, either members of metamorphic layered mafic-ultramafic intrusions or simply in association with ultramafic rocks (peridotite or pyroxenite).

Four metamorphic stages have been recognized for high-grade units in the Dabie–Sulu orogenic belt (Ernst & Liou, 1999; Zheng *et al.*, 2003; Li *et al.*, 2004): (1) peak UHP coesite/diamond eclogite-facies, recorded by the occurrence of coesite or diamond, with metamorphic temperatures of ~ 800 – 700 °C at > 2.8 GPa; (2) HP quartz eclogite facies recrystallization, represented by the coexistence of garnet and omphacite with quartz instead of coesite, with metamorphic conditions of ~ 750 – 600 °C and 2.4–1.2 GPa; (3) HP granulite facies overprinting, represented by the occurrence of orthopyroxene or plagioclase, with metamorphic conditions of ~ 850 – 750 °C and 2.0–1.0 GPa; (4) amphibolite-facies retrogression, indicated by the occurrence of various symplectites such as amphibole + sodic plagioclase after omphacite from eclogite, with P – T conditions of ~ 600 – 450 °C and 1.0–0.6 GPa. The zones of different metamorphic grades crop out heterogeneously along the orogenic belt, which is generally bounded by blueschist-facies zones in the south and greenschist-facies zones in the north (Zheng *et al.*, 2005).

The CCSD site is located near Maobei village ($34^{\circ}25'N$, $118^{\circ}40'E$), ~ 17 km south-west of Donghai in the south-western part of the Sulu orogen (Fig. 1). Major goals of the CCSD, as outlined by Xu *et al.* (1998), include (1) revealing the crustal structure of convergent plate boundaries, (2) providing constraints on crust–mantle interactions and mantle behaviour during deep subduction of continental crust, and (3) investigating fluid evolution during UHP metamorphism. The CCSD-MH was completed at its final depth of 5138 m in March 2005. It provides a rare opportunity to sample various UHP rocks continuously from great depths.

Metamorphic rocks recovered are various types of gneiss, eclogite, amphibolite, marble and peridotite. Coesite was found as inclusions within zircon from both gneiss and eclogite (Liu *et al.*, 2001, 2002, 2004a,b,c; Zhang *et al.*, 2006), indicating that both eclogite and gneiss have been subjected to *in situ* UHP metamorphism. Microdiamond was identified in eclogite from Maobei, the CCSD-MH site (Xu *et al.*, 2003, 2005). The P – T estimates of 675–815 °C and 3.1–4.4 GPa were obtained for the eclogites at depths of 0–2050 m from the MH of CCSD (Liu *et al.*, 2004a; Zhang *et al.*, 2006). SHRIMP U–Pb dating was made for coesite-bearing domains of zircon from the gneisses of the CCSD cores (Liu *et al.*, 2004b,c; Liu & Xu, 2004), yielding ages of 234–226 Ma for the UHP metamorphic event and *c.* 750–780 Ma for the igneous

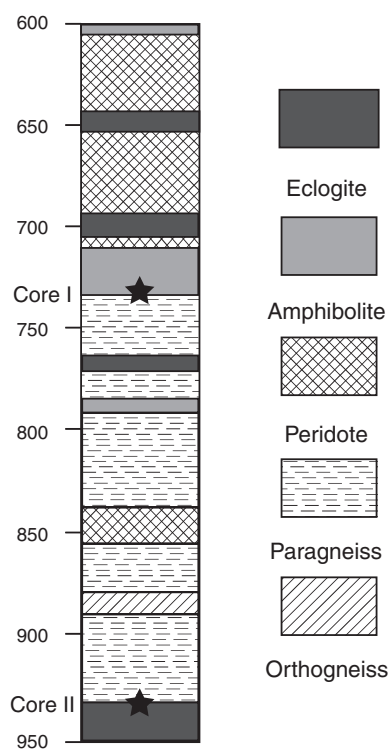


Fig. 2. Lithological profile of Chinese Continental Scientific Drilling main hole from 600 to 950 m (revised after Zhang *et al.*, 2006).

protoliths. These dates are consistent with known results from multi-method geochronological studies of UHP metamorphic rocks exposed at the surface along the Dabie–Sulu orogenic belt (e.g. Ames *et al.*, 1996; Hacker *et al.*, 1998, 2000; Li *et al.*, 1999, 2000, 2004; Zheng *et al.*, 2003, 2004; Wu *et al.*, 2006).

So far the recovered lithologies from the CCSD-MH mainly comprise gneisses with minor eclogite, amphibolite, peridotite, marble, schist, mylonite and cataclasite (Xu, 2004). This study uses two core segments composed of interlayered gneiss, eclogite and garnet amphibolite (Fig. 2). They are from depths of 734.21–737.16 and 929.67–932.86 m, respectively, and named as the first and second core segments. A general description of petrology for 0 to 2000 m cores has been presented by Liu *et al.* (2004a), Su *et al.* (2005) and Zhang *et al.* (2006).

The first segment (02CCSD-I) comprises a transition between eclogite and gneiss from depths of 734.21–737.16 m (Fig. 2). The eclogite shows porphyroblastic texture with garnet as the porphyroblast, and has a mineral paragenesis of garnet + omphacite + rutile + zircon $\pm$ phengite $\pm$ quartz. The most prominent microstructure is symplectite produced by amphibolite-facies retrogression of garnet and omphacite (Fig. 3a,b). Omphacite is generally replaced by amphibole and sodic plagioclase symplectite, and garnet by amphibole and plagioclase symplectite; rutile

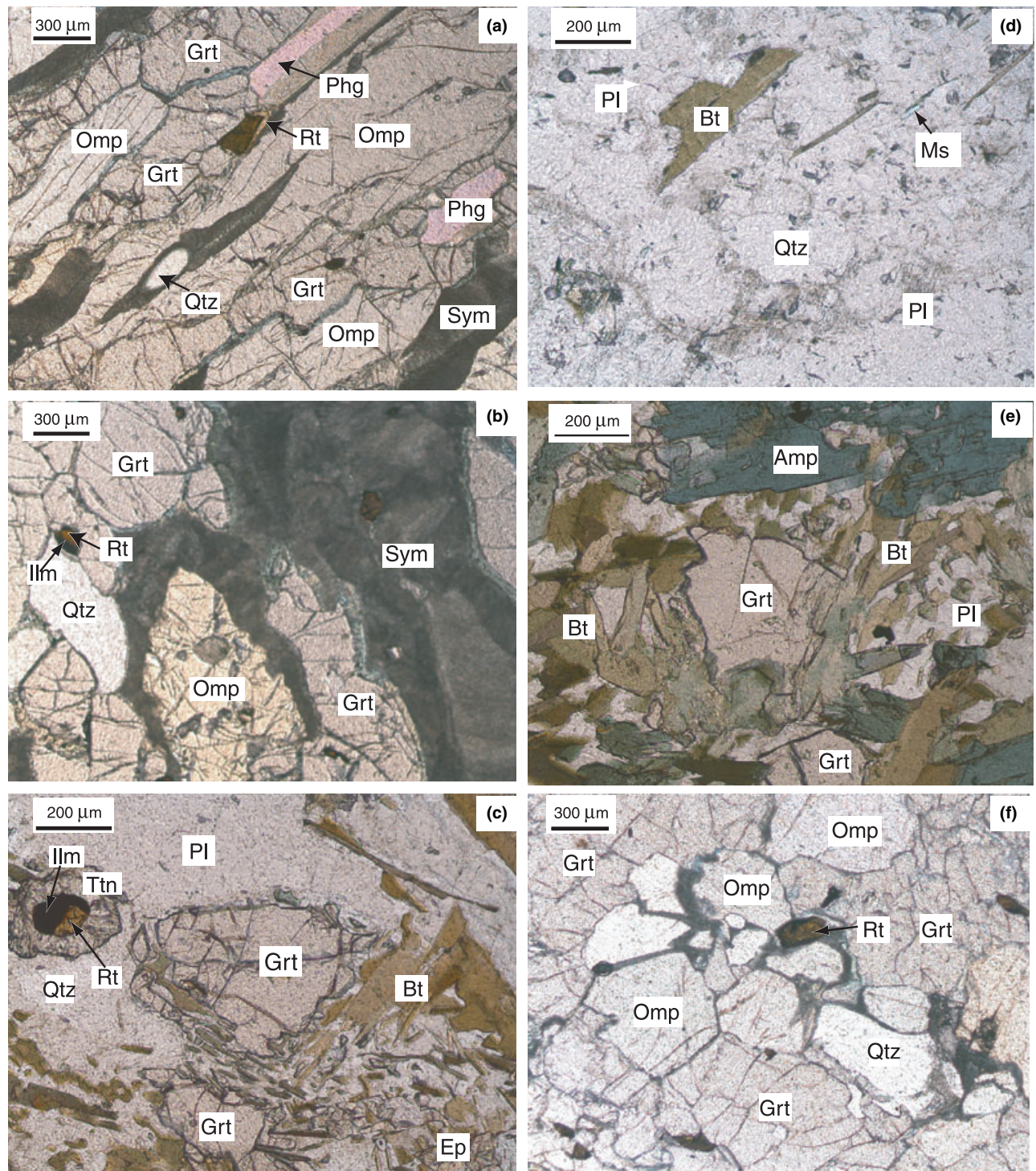


Fig. 3. Photomicrographs of eclogite, gneiss and garnet amphibolite from the Chinese Continental Scientific Drilling (CCSD) main hole in plane polarized light. (a) Eclogite (02CCSD-I10A, 735.20 m) consists of garnet, omphacite, phengite, quartz and rutile. Some of omphacite grains are replaced by symplectite, garnet is commonly rimmed by symplectite. (b) Eclogite (02CCSD-I6A, 736.01 m), is composed of garnet, omphacite, quartz and rutile. Abundant symplectite was formed after omphacite, rutile is rimmed by ilmenite. (c) Gneiss (02CCSD-I3A, 736.74 m) contains garnet, quartz, plagioclase, biotite, epidote, ilmenite, rutile and titanite. Ilmenite is rimmed by titanite, rutile occurs as a relict mineral. (d) Gneiss (02CCSD-II10A, 930.16 m) consists of quartz, plagioclase, biotite and muscovite. (e) Garnet amphibolite (02CCSD-II7A, 930.74 m) is composed of garnet, amphibole, biotite and plagioclase. (f) Eclogite (02CCSD-II3A, 932.03 m) contains garnet, omphacite, quartz and rutile. Garnet and omphacite are commonly rimmed by symplectite. Mineral abbreviations: Grt = garnet, Omp = omphacite, Phg = phengite, Sym = symplectite, Qtz = quartz, Rt = rutile, Ilm = ilmenite, Ttn = titanite, Amp = amphibole, Bt = biotite, Pl = plagioclase, Ep = epidote, Ms = muscovite.

is commonly rimmed by ilmenite. The degree of retrograde metamorphism apparently increases with decreasing distance from the contact zone between eclogite and gneiss. For example, the eclogite sample 02CCSD-I6A (Fig. 3b) adjacent to gneiss has more abundant symplectite than the sample 02CCSD-I10A (Fig. 3a) far away from gneiss. The gneiss mainly consists of quartz, plagioclase, garnet, epidote, biotite and amphibole, with minor apatite, rutile, ilmenite and titanite. In places it looks like a retrograde eclogite (Fig. 3c), with relict garnet that is rimmed by a symplectite of amphibole and plagioclase, and relict rutile that was replaced by ilmenite and titanite, but ~50% quartz + feldspar defines the rock as a felsic gneiss.

The second core segment (02CCSD-II) consists of a transition from gneiss, garnet amphibolite to eclogite from depths of 929.67–932.86 m (Fig. 2). The gneiss has an amphibolite-facies mineral assemblage, where plagioclase, K-feldspar, quartz, biotite, muscovite and amphibole are the principal phases, with a small amount of residual garnet (Fig. 3d). The garnet amphibolite lies between gneiss and eclogite, and is the product of almost complete retrogression of eclogite. The garnet amphibolite is generally composed of amphibole, quartz, garnet, plagioclase, apatite, epidote and biotite. Abundant symplectite after the primary omphacite and large amounts of residual garnet can be observed in the garnet amphibolite that is close to eclogite. In contrast, larger amphibole grains in symplectite after omphacite, less residual garnet and more biotite, and titanite rims on ilmenite occur in the garnet amphibolite adjacent to gneiss (Fig. 3e). Mineral paragenesis of the eclogite is garnet, omphacite and quartz, with small amounts of phengite, rutile and ilmenite. Garnet and omphacite are commonly surrounded by retrograde metamorphic rims; rutile is commonly rimmed by ilmenite (Fig. 3f).

ANALYTICAL METHODS

Mineral grains were separated from the rock samples by conventional magnetic and heavy liquid techniques followed by manual picking under a binocular microscope. Oxygen isotope analysis of mineral separates was carried out by the laser fluorination technique using a 25 W CO₂ laser MIR-10 at University of Science and Technology of China in Hefei, China. Minerals with weight of ~1.5–2.0 mg were reacted with BrF₅ at vacuum, and obtained O₂ was directly transferred to a mass spectrometer Delta+ for O isotope ratio measurement (Zheng *et al.*, 2002). The ¹⁸O/¹⁶O ratios were reported in the δ¹⁸O notation relative to the VSMOW standard. A number of replicate analyses give a reproducibility of more than ±0.1‰ for routine analysis. Three international standards were used during the laser fluorination analyses: (1) δ¹⁸O = 5.8‰ for garnet UWG-2 (Valley *et al.*, 1995); (2) δ¹⁸O = 10.0‰ for zircon 91500 (Zheng *et al.*, 2004); (3) δ¹⁸O = 11.11‰ for quartz

GBW04409 (Zheng *et al.*, 1998). Mineral-pair O isotopic temperatures are calculated using the fractionation curves of Zheng (1991, 1993a,b), assuming preservation of isotope equilibration at the scale of sample measurement. Temperature errors are estimated to be ~30–50 °C in terms of the analytical uncertainties in mineral δ¹⁸O determination and fractionation curve calibration. Judgment and interpretation of O isotope equilibrium or disequilibrium between coexisting minerals are based on measured fractionation values and resultant sequence of O isotope temperatures in combination with rates of O diffusion in concerned minerals and corresponding sequence of closure temperatures (e.g. Giletti, 1986; Zheng & Fu, 1998; Zhao *et al.*, 2004).

Fourier Transform Infrared Spectroscopy (FTIR) analysis of nominally anhydrous minerals was carried out between wavenumbers of 400 and 4000 cm⁻¹ using a Nicolet 550 FTIR spectrometer at Chinese University of Geosciences in Wuhan, China. The samples were made into doubly polished sections with thickness of 0.1–0.5 mm. Before analysis, sections were dipped in ethanol for more than 24 h, followed by repeated cleaning with ethanol and distilled water. In order to remove the surface and crack absorbed water, sections were heated in an oven at ~100 °C for more than 6 h (e.g. Su *et al.*, 2002; Katayama & Nakashima, 2003; Xia *et al.*, 2005). The samples were measured by unpolarized radiation with an IR light source, KBr beam-splitter and an MCT detector, at room temperature. Sixty-four scans were averaged for each analysis with a resolution of 8 cm⁻¹. The background was recorded before analysing each section. We measured optically crack- and inclusion-free sample areas with an aperture of 50 × 50 to 70 × 70 μm.

Water content was calculated by the Lambert–Beer's law as follows:

$$C_{\text{OH}} = \frac{1}{I\gamma d} \int_{\nu_1}^{\nu_2} K(\nu) d\nu,$$

where C_{OH} is the concentration of water in analysed minerals, expressed as moles per litre (mol l⁻¹), $K(\nu)$ is the absorption intensity (absorbance) of the water as a function of wavenumber ν , I is integral molar absorption coefficient, γ is the orientation factor, which depends on crystallographic anisotropy, and d is the sample thickness. Because the precision of thickness in the same section is <10%, the average value was used for different grains from the same samples. The integral molar absorption coefficients of garnet and omphacite are from Bell *et al.* (1995) and Katayama *et al.* (2006), respectively. An orientation factor of 1/3 is used for omphacite.

Uncertainty in the calculated water content comes from: (1) the baseline correction; (2) calculation of the integrated area; (3) minor difference in thickness for different grains in the same section; (4) absorption coefficients due to difference in composition between the studied minerals and those used by Bell *et al.*

(1995) and Katayama *et al.* (2006). The last effect is very small for garnet because the differences among even pure end-member garnet are < 10‰ (Rossman & Aines, 1991; Bell *et al.*, 1995). On this basis, the overall uncertainties are estimated to be ~20‰ for garnet and 20–40‰ for omphacite.

RESULTS

Mineral O isotopes

The O isotope composition of mineral separates for both eclogite and gneiss are presented in Table 1. The eclogite samples from the first core segment have $\delta^{18}\text{O}$ values of 4.5–7.3‰ for quartz, 1.0–3.8‰ for garnet and 1.4–4.0‰ for omphacite, whereas those from the second core segment exhibit relatively low $\delta^{18}\text{O}$ values of –0.4 to 0.4‰ for quartz, –4.5 to –3.3‰ for garnet, and –4.6 to –2.6‰ for omphacite. Likewise, the gneiss samples from the first core segment have $\delta^{18}\text{O}$ values of 1.2–2.4‰ for quartz, –2.7 to –1.9‰ for garnet, –2.6 to –2.0‰ for epidote and –3.6 to –2.6‰ for biotite, whereas those from the second core segment show relatively low $\delta^{18}\text{O}$ values of –0.4 to 0.2‰ for quartz, –4.1 to –2.7‰ for muscovite and –3.8 to –3.6‰ for garnet. Because the eclogite is mainly composed of garnet and omphacite, the whole-rock $\delta^{18}\text{O}$ values are estimated to ~1.0–4.0‰ and –4.5 to –2.6‰, respectively, for the eclogite from the first and second core segments. The $\delta^{18}\text{O}$ values from the first core segment are significantly higher than those from the second core segment (Fig. 4).

Figures 5 and 6 show two O isotope profiles of minerals in the eclogites and gneisses from the first and second core segments, respectively. The O isotope composition varies with spatial distribution; mineral $\delta^{18}\text{O}$ values for both eclogite and gneiss in the first core segment are significantly higher than those in the second core segment. Apparently, both eclogite and gneiss from the second core segment are characterized by relatively homogeneous $\delta^{18}\text{O}$ distribution (Fig. 6), whereas those from the first core segment are significantly heterogeneous in mineral $\delta^{18}\text{O}$ values, as indicated by not only large $\delta^{18}\text{O}$ difference between eclogite and gneiss, but also variation in $\delta^{18}\text{O}$ among eclogites (Fig. 5).

For the first core segment, the eclogites show an abrupt variation in mineral $\delta^{18}\text{O}$ values at ~1 m, with a progressive decrease in $\delta^{18}\text{O}$ towards the boundary between eclogite and gneiss (Fig. 5). Eclogites 02CCSD-I5A, I6A and I7A adjacent to gneiss have $\delta^{18}\text{O}$ values of 1.0–1.7‰ for garnet and 1.4–2.1‰ for omphacite, whereas eclogites 02CCSD-I8A to I14A far away from the gneiss have $\delta^{18}\text{O}$ values of 3.0–3.8‰ and 2.8–4.0‰ for garnet and omphacite, respectively. In contrast, the gneisses exhibit a progressive increase in $\delta^{18}\text{O}$ towards the boundary. The gneisses have different isotope compositions with negative $\delta^{18}\text{O}$ values of –2.7 to –1.9‰ for garnet, which are significantly lower than those of the associated eclogites (Table 1; Fig. 5).

For the second core segment (Fig. 6), a garnet amphibolite zone separates the eclogite from the gneiss. Because of the difficulty in recovering mineral separates from the amphibolite, only a few minerals were analysed for O isotopes. The available results show that the eclogites exhibit slight increase in $\delta^{18}\text{O}$ values for garnet, omphacite, muscovite and rutile values towards the boundary between eclogite and amphibolite, but no considerable change occurs in quartz $\delta^{18}\text{O}$ values. Similarly, the gneisses also show a progressive increase in mineral $\delta^{18}\text{O}$ values towards the boundary between amphibolite and gneiss. The gneisses generally have similar $\delta^{18}\text{O}$ values to the eclogites, but quartz and feldspar from the amphibolite have increased $\delta^{18}\text{O}$ values relative to those in the adjacent gneisses. One amphibole from the amphibolite has a lower $\delta^{18}\text{O}$ value than omphacite from the eclogite, suggesting that aqueous fluid for amphibolite-facies retrogression was depleted in ^{18}O relative to the precursor omphacites.

The mineral-pair O isotope fractionations are in both equilibrium and disequilibrium in the eclogites, and O isotope fractionations between quartz and the other minerals in the gneisses show both equilibrium and disequilibrium (Fig. 4). The O isotope temperatures for the quartz–mineral pairs span wide ranges (Table 1), and many of them are too low to represent eclogite-facies conditions (Fig. 4). The O isotope geothermometry for the eclogites from the quartz–garnet pair yields temperatures of 575–770 °C, which are slightly lower than, but close to the temperatures of 600–750 °C responsible for eclogite-facies metamorphic conditions, indicating attainment and preservation of O isotope equilibrium between quartz and garnet at eclogite-facies conditions. However, the quartz–omphacite, quartz–phengite and quartz–rutile pairs from the eclogites yield temperatures of 380–705, 375–595 and 395–525 °C, respectively.

On the other hand, O isotope geothermometry for the gneisses from quartz–feldspar, quartz–muscovite, quartz–biotite and quartz–epidote pairs give temperatures of 425–565, 355–660, 390–475 and 380–455 °C, respectively (Table 1). These isotopic temperatures are generally compatible with O isotope equilibrium under amphibolite-facies conditions. However, the higher isotopic temperatures of 560–730 °C are obtained for the quartz–garnet pair (Table 1). This indicates that the O isotope composition of garnet is not significantly affected by amphibolite-facies retrogression during exhumation. In either case, the bulk O isotope system of both eclogite and gneiss remains relatively closed with no considerable modification by external fluids, and thus preserves protolith $\delta^{18}\text{O}$ values. Both eclogite and gneiss are variably depleted in ^{18}O relative to the normal mantle $\delta^{18}\text{O}$ values of 5.7 ± 0.5 ‰ (Hoefs, 2004), consistent with previous recognition that their protoliths experienced meteoric–hydrothermal alteration at high temperatures (Zheng *et al.*, 1998, 1999).

Table 1. Oxygen isotope compositions of minerals in ultrahigh-pressure eclogites and gneisses from CCSD-MH and estimated temperature.

Sample number	Depth (m)	Mineral	$\delta^{18}\text{O}$ (‰)	Pair ^a	$\Delta^{18}\text{O}$ (‰)	T (°C)
Core I						
02CCSD-I1A	737.16	Quartz	1.8			
Gneiss		Garnet	-2.6	Qtz–Grt	4.4	560
		Epidote	-2.4	Qtz–Ep	4.2	400
		Biotite	-3.5	Qtz–Bt	5.3	425
02CCSD-I2A	736.93	Quartz	1.6			
Gneiss		Garnet	-2.7	Qtz–Grt	4.3	570
		Epidote	-2.6	Qtz–Ep	4.2	400
		Biotite	-3.6	Qtz–Bt	5.2	440
02CCSD-I3A	736.74	Quartz	1.2			
Gneiss		Garnet	-2.4	Qtz–Grt	3.6	665
		Epidote	-2.5	Qtz–Ep	3.7	455
		Biotite	-3.6	Qtz–Bt	4.8	475
02CCSD-I4A	736.46	Quartz	2.4			
Gneiss		Garnet	-1.9	Qtz–Grt	4.3	570
		K-feldspar	0.8	Qtz–Kfs	1.6	495
		Epidote	-2.0	Qtz–Ep	4.4	380
		Biotite	-2.6	Qtz–Bt	5.0	455
		Rutile	-5.6	Qtz–Rt	8.0	415
02CCSD-I5A	736.28	Quartz	4.5			
Eclogite		Omphacite	1.4	Qtz–Omp	3.1	565
		Garnet	1.0	Qtz–Grt	3.5	680
		Rutile	-3.0	Qtz–Rt	7.5	440
02CCSD-I6A	736.01	Quartz	4.6			
Eclogite		Omphacite	1.5	Qtz–Omp	3.1	565
		Garnet	1.1	Qtz–Grt	3.5	680
		Rutile	-3.0	Qtz–Rt	7.6	435
02CCSD-I7A	735.87	Quartz	5.3			
Eclogite		Omphacite	2.1	Qtz–Omp	3.2	550
		Garnet	1.7	Qtz–Grt	3.6	665
		Phengite	2.3	Qtz–Phg	3.0	520
		Rutile	-2.5	Qtz–Rt	7.8	425
02CCSD-I8A	735.52	Omphacite	2.8			
Eclogite		Garnet	3.3			
		Phengite	3.6			
		Rutile	-1.2			
02CCSD-I9A	735.37	Quartz	6.5			
Eclogite		Omphacite	2.8	Qtz–Omp	3.7	480
		Garnet	3.0	Qtz–Grt	3.5	680
		Phengite	3.6	Qtz–Phg	2.9	540
		Rutile	-0.9	Qtz–Rt	7.4	450
02CCSD-I10A	735.20	Omphacite	3.3			
Eclogite		Garnet	3.3			
		Phengite	3.9			
		Rutile	-0.5			
02CCSD-I11A	735.02	Quartz	7.3			
Eclogite		Omphacite	3.4	Qtz–Omp	3.9	455
		Garnet	3.3	Qtz–Grt	4.0	610
		Phengite	3.6	Qtz–Phg	3.7	420
		Rutile	-0.3	Qtz–Rt	7.6	435
02CCSD-I12A	734.78	Quartz	6.8			
Eclogite		Omphacite	3.8	Qtz–Omp	3.0	585
		Garnet	3.6	Qtz–Grt	3.2	730
		Phengite	4.2	Qtz–Phg	2.6	595
		Rutile	0.6	Qtz–Rt	6.2	525
02CCSD-I13A	734.39	Omphacite	3.2			
Eclogite		Garnet	3.6			
		Rutile	0.1			
02CCSD-I14A	734.13	Omphacite	4.0			
Eclogite		Garnet	3.8			
		Rutile	0.5			
		Core II				
02CCSD-II1A	932.81	Quartz	0.1			
Eclogite		Omphacite	-2.6	Qtz–Omp	2.7	640
		Garnet	-4.1	Qtz–Grt	4.2	585
		Phengite	-2.9	Qtz–Phg	3.0	520
		Rutile	-8.3	Qtz–Rt	8.4	395
02CCSD-II1(2)A	932.49	Quartz	0.1			
Eclogite		Omphacite	-3.1	Qtz–Omp	3.2	550
		Garnet	-3.8	Qtz–Grt	3.9	625
		Phengite	-2.9	Qtz–Phg	3.0	520
		Rutile	-7.9	Qtz–Rt	8.0	410
	932.21	Quartz	-0.3			

Table 1. *Cont'd*

Sample number	Depth (m)	Mineral	$\delta^{18}\text{O}$ (‰)	Pair ^a	$\Delta^{18}\text{O}$ (‰)	T (°C)
02CCSD-II1(2)A		Omphacite	-4.1	Qtz–Omp	3.8	470
Eclogite		Garnet	-4.5	Qtz–Grt	4.2	585
		K-feldspar	-2.3	Qtz–Kfs	2.0	390
		Plagioclase	-2.5	Qtz–Pl	2.2	360
		Rutile	-8.0	Qtz–Rt	7.7	430
02CCSD-II3A	932.03	Quartz	0.4			
Eclogite		Omphacite	-3.9	Qtz–Omp	4.3	410
		Garnet	-3.9	Qtz–Grt	4.3	575
		Phengite	-3.7	Qtz–Phg	4.1	375
		Rutile	-7.9	Qtz–Rt	8.3	400
02CCSD-II4(1)A	931.74	Quartz	0.0			
Eclogite		Omphacite	-4.6	Qtz–Omp	4.6	380
		Garnet	-4.1	Qtz–Grt	4.1	600
		Rutile	-8.0	Qtz–Rt	8.0	415
02CCSD-II4(2)A	931.56	Quartz	-0.4			
Eclogite		Omphacite	-3.4	Qtz–Omp	3.0	585
		Garnet	-3.7	Qtz–Grt	3.3	715
		Rutile	-7.0	Qtz–Rt	6.6	495
02CCSD-II5A	931.33	Quartz	-0.3			
Eclogite		Omphacite	-3.3	Qtz–Omp	3.0	585
		Garnet	-3.3	Qtz–Grt	3.0	770
		Rutile	-7.1	Qtz–Rt	6.8	485
02CCSD-II6A	931.11	Garnet amphibolite				
02CCSD-II7A	930.74	Amphibole	-4.2			
02CCSD-II8A	930.52	Garnet amphibolite				
Gneiss		Quartz	0.7			
		Garnet	-3.5	Qtz–Grt	4.2	585
		K-feldspar	-0.8	Qtz–Kfs	1.5	530
		Plagioclase	-1.0	Qtz–Pl	1.7	475
		Biotite	-5.2	Qtz–Bt	5.9	380
02CCSD-II9A	930.32	Quartz	-0.4			
Gneiss		K-feldspar	-1.8	Qtz–Kfs	1.4	565
		Plagioclase	-1.9	Qtz–Pl	1.5	540
		Muscovite	-2.7	Qtz–Ms	2.3	660
		Garnet	-3.6	Qtz–Grt	3.2	730
02CCSD-II10A	930.16	Quartz	-0.1			
Gneiss		K-feldspar	-1.9	Qtz–Kfs	2.0	390
		Plagioclase	-2.0	Qtz–Pl	1.9	430
		Muscovite	-4.0	Qtz–Ms	3.9	400
		Amphibole	-3.9	Qtz–Amp	3.8	560
		Biotite	-5.9	Qtz–Bt	5.8	390
02CCSD-II11A	929.95	Magnetite	-6.9	Qtz–Mt	6.8	600
		Quartz	0.2			
		K-feldspar	-1.5	Qtz–Kfs	1.7	465
02CCSD-II12A	929.72	Plagioclase	-1.7	Qtz–Pl	1.9	430
		Muscovite	-4.1	Qtz–Ms	4.3	355
		Quartz	-0.3			
Gneiss		Muscovite	-3.2	Qtz–Ms	2.9	540
		Garnet	-3.8	Qtz–Grt	3.5	680

^aQtz, quartz; Kfs, K-feldspar; Pl, plagioclase (An = 10); Phg, phengite; Omp, omphacite (Jd₄₀Di₆₀); Ep, epidote; Amp, amphibole; Bt, biotite; Grt, garnet; Rt, rutile; Mt, magnetite; Ms, muscovite.

Water content

The FTIR spectra of garnet exhibit several absorption bands in the typical OH⁻ stretching vibration region (3000–3700 cm⁻¹) (Table 2; Fig. 7), that can be categorized into four groups: (I) 3400–3450 cm⁻¹; (II) 3510–3550 cm⁻¹; (III) 3570–3600 cm⁻¹; (IV) 3610–3630 cm⁻¹. Previous FTIR investigations of natural and synthesized garnet show that the above four groups are the common OH⁻ absorption bands (Aines & Rossman, 1984; Rossman *et al.*, 1989; Geiger *et al.*, 1991; Rossman & Aines, 1991; Bell & Rossman, 1992; Beran *et al.*, 1993; Langer *et al.*, 1993; Snyder *et al.*, 1995; Lu & Keppler, 1997; Matsyuk *et al.*, 1998; Withers *et al.*, 1998; Su *et al.*, 2002), in which groups

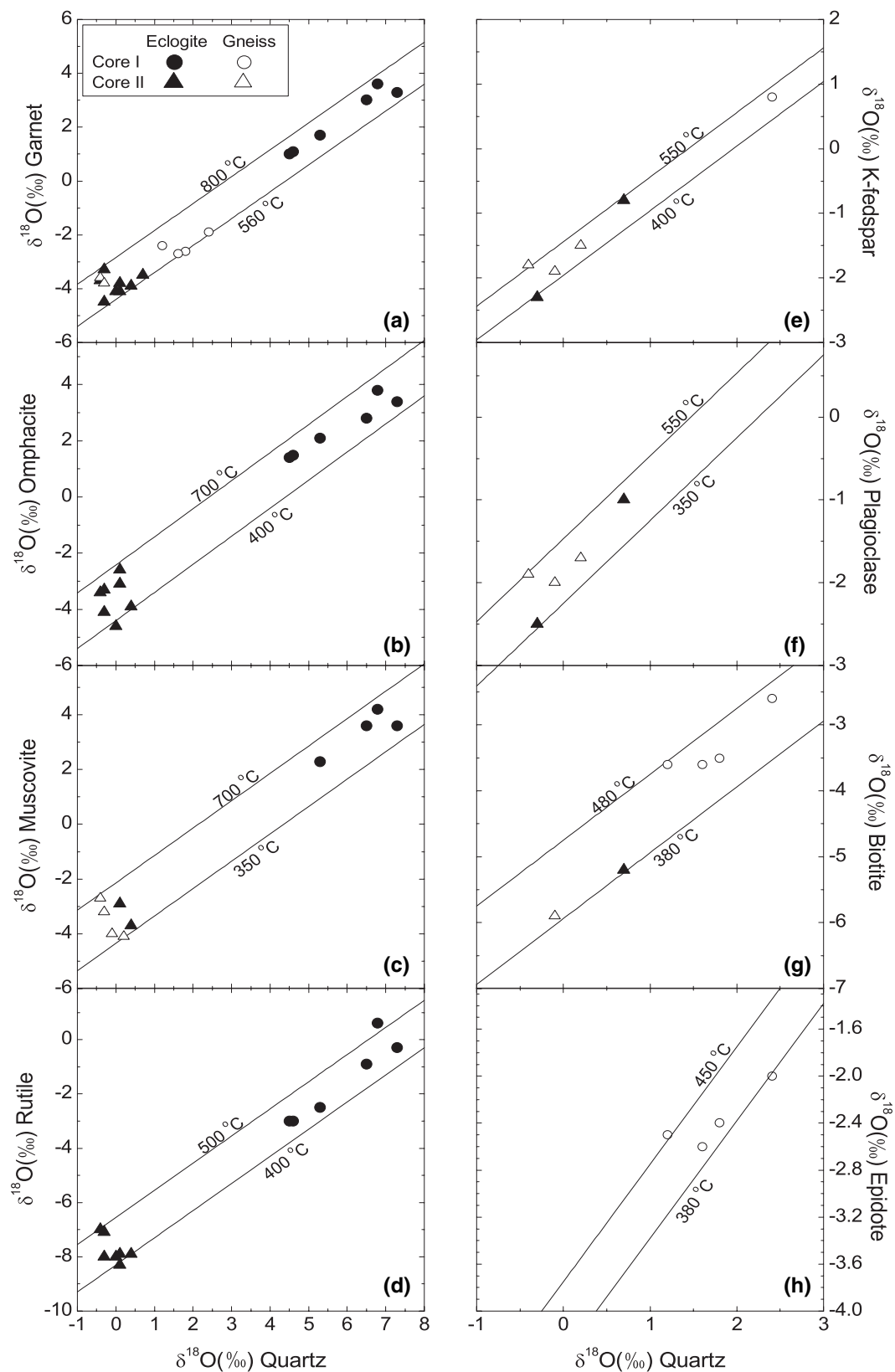


Fig. 4. Plots of the O isotope composition of quartz v. coexisting minerals in eclogites and gneisses from the Chinese Continental Scientific Drilling main hole. Fractionation lines at different temperatures are drawn by applying the theoretical calibrations of Zheng (1991, 1993a,b).

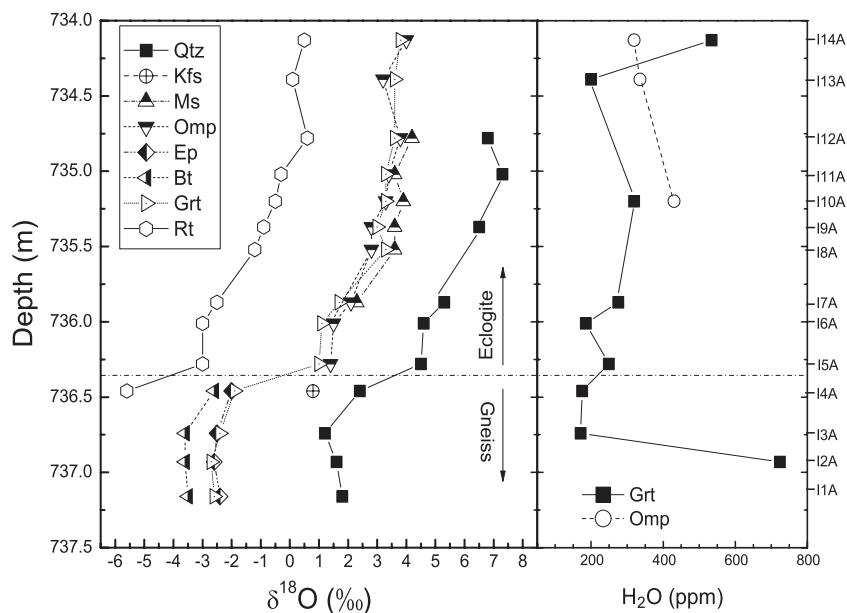


Fig. 5. Profiles of $\delta^{18}\text{O}$ values in the core segment 02CCSD-I and corresponding hydroxyl content in garnet and omphacite.

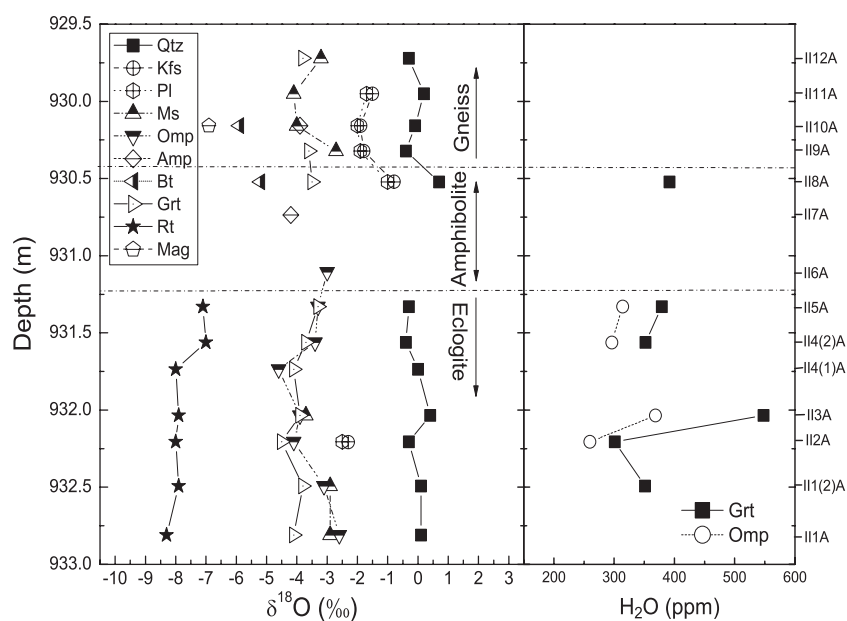


Fig. 6. Profiles of $\delta^{18}\text{O}$ values in the core segment 02CCSD-II and corresponding hydroxyl content in garnet and omphacite.

II, III and IV are generally considered the structural OH^- absorption bands, whereas group I is accounted for by the presence of molecular water such as sub-microscopic fluid inclusions (Rossman *et al.*, 1989; Bell & Rossman, 1992; Beran *et al.*, 1993; Langer *et al.*, 1993; Matsyuk *et al.*, 1998; Katayama & Nakashima, 2003).

Garnet in eclogites from the two core segments shows hydroxyl absorption at $3000\text{--}3800\text{ cm}^{-1}$, which consists of an intense band at 3620 cm^{-1} and a weak broad band at $3400\text{--}3450\text{ cm}^{-1}$ (Fig. 7a,d), two least intense bands at $3570\text{--}3600$ and $3510\text{--}3550\text{ cm}^{-1}$ are also observed in some of grains. Only one grain was investigated because

of the general lack of fresh garnet in garnet amphibolite from the second core segment; the result shows two obvious absorption bands at 3425 and 3615 cm^{-1} as well as a weak band at 3565 cm^{-1} (Fig. 7c), and the relative band intensity at 3425 cm^{-1} is higher than those of eclogite and gneiss. On the other hand, garnet in the gneisses from the first core segment exhibit three absorption bands, that are a weak band at $3400\text{--}3450\text{ cm}^{-1}$, an intense band at 3585 cm^{-1} and a moderate band $\sim 3620\text{ cm}^{-1}$ (Fig. 7b).

Fourier Transform Infrared Spectroscopy for omphacite shows four hydroxyl absorption bands in the regions of $3445\text{--}3455$, $3510\text{--}3520$, $3605\text{--}3625$ and

Table 2. Fourier Transform Infrared Spectroscopy analysis of garnet in ultrahigh-pressure eclogite and gneiss from two Chinese Continental Scientific Drilling core segments.

Sample	Grain	Thickness (mm)	Band (cm ⁻¹)				Area (cm ⁻¹)	H ₂ O (p.p.m. wt)	Ave. H ₂ O (p.p.m. wt)
			I 3400–3450	II 3510–3550	III 3570–3600	IV 3610–3630			
02CCSD-I									
I2A	1	0.20	3405		3583	3620	6	214	724
	2		3437		3583	3618	24	858	
	3		3430		3589	3627	32	1144	
	4		3436		3588		19	679	
I3A	1	0.25	3444		3583	3626	6	171	171
I4A	1	0.30	3403	3524		3634	4	96	175
	2		3416		3630	7	167		
	3		3401		3595	3631	11	263	
I5A	1	0.12	3463			3616	6	365	249
	2		3392	3517		3630	6	365	
	3					3633	2	122	
	4		3408			3636	3	182	
	5		3414			3635	3	182	
	6		3441			3621	3	182	
	7		3429			3640	5	304	
	8		3438			3628	4	243	
	9		3433	3528		3627	4	243	
	10		3440	3537		3621	5	304	
I6A	1	0.29		3539		3637	2	50	185
	2		3462			3629	10	251	
	3		3421			3629	18	452	
	4				3578	3639	3	75	
	5		3413	3541		3628	4	100	
	6		3402			3635	9	226	
	7		3411			3629	7	176	
	8		3455			3625	6	151	
I7A	1	0.19	3441			3637	5	187	275
	2		3408			3627	4	150	
	3		3429	3506		3625	8	300	
	4			3496		3630	9	337	
	5		3426			3634	9	337	
	6		3452	3522		3633	5	187	
	7		3394	3545		3635	8	300	
	8		3414			3634	5	187	
I10A	9	0.26	3404			3635	13	487	319
	1		3474	3551		3629	4	110	
	2		3456			3632	7	193	
	3		3445			3627	12	331	
	4		3440			3626	12	331	
	5		3452	3515		3620	9	248	
	6		3445	3546		3622	17	468	
	7		3450			3626	12	331	
	8		3434			3626	12	331	
	9		3465			3610	18	496	
I13A	10	0.35	3452			3625	13	358	200
	1		3432	3550		3631	7	144	
	2		3445		3581	3633	15	309	
	3		3393			3621	16	330	
	4		3423			3628	5	103	
	5		3423			3630	7	144	
	6		3431			3627	8	165	
	7		3421			3623	13	268	
	8		3421			3623	14	289	
	9		3404			3635	4	83	
I14A	10	0.65	3417			3614	8	165	534
	1		3459			3608	39	434	
	2		3428	3541		3608	57	635	
02CCSD-II									
II1(2)A	1	0.22	3438			3637	7	230	351
	2		3461			3634	9	295	
	3		3432			3626	11	361	
	4		3423			3633	13	426	
	5		3455			3638	11	361	
	6		3453			3625	10	328	
	7		3429			3631	13	426	
	8		3437			3630	11	361	
	9		3438			3632	10	328	
	10		3463			3633	12	393	
II2A	1	0.30	3419		3583	3628	20	481	301
	2		3426		3594	3636	13	313	
	3		3431		3578	3628	13	313	

Table 2. *Cont'd*

Sample	Grain	Thickness (mm)	Band (cm ⁻¹)				Area (cm ⁻¹)	H ₂ O (p.p.m. wt)	Ave. H ₂ O (p.p.m. wt)
			I 3400–3450	II 3510–3550	III 3570–3600	IV 3610–3630			
II3A	4	0.26	3440	3528	3580	3617	8	192	548
	5		3458		3571	3630	27	649	
	6		3435		3591	3624	16	385	
	7		3429			3627	16	385	
	8		3403			3633	4	96	
	9		3397			3624	5	120	
	10		3461			3633	3	72	
	1		3416			3621	12	336	
	2		3425			3632	16	449	
	3		3412			3627	30	841	
II4(2)A	4	0.34	3421		3563	3609	22	617	352
	5		3414			3609	16	449	
	6		3406		3597	3649	24	673	
	7		3406		3600	3626	20	561	
	8		3390		3603	3638	25	701	
	9		3428		3576	3632	15	421	
	10		3427			3611	16	449	
	1		3444			3628	11	231	
	2		3430			3614	27	566	
	3		3450	3556		3610	8	168	
II5A	4	0.31	3450	3550		3629	14	294	379
	5		3454			3623	17	356	
	6		3435	3553		3610	14	294	
	7		3455			3636	10	210	
	8		3405		3582	3619	37	776	
	9		3450	3556		3610	16	335	
	10		3444	3539		3608	14	294	
	1		3426		3577	3630	19	440	
	2		3418		3573		21	486	
	3		3423		3574	3627	17	393	
II8A	4	0.26	3415	3555		3603	18	417	392
	5		3432		3561	3625	10	231	
	6		3438		3600	3636	10	231	
	7		3454			3625	11	255	
	8		3429		3579	3634	25	579	
	1		3425		3565	3615	14	392	

3670 cm⁻¹ (Fig. 8). The 3445–3455 cm⁻¹ band is typically the most intense, which is similar to the previous reports in both synthetic and natural clinopyroxene (Skogby *et al.*, 1990; Smyth *et al.*, 1991; Bromiley & Keppler, 2004; Bromiley *et al.*, 2004a).

Fourier Transform Infrared Spectroscopy for garnet yields 50–653 p.p.m. H₂O (by weight) for the eclogites from the first core segment, 72–841 p.p.m. H₂O for the eclogites from the second core segment, and 392 p.p.m. H₂O for the garnet amphibolite (Table 2). On the other hand, hydroxyl contents in garnet from the gneisses from the first core segment range from 96 to 1144 p.p.m. As shown in Table 3, the integral hydroxyl absorbance of omphacite yields 139–751 p.p.m. H₂O and 147–530 p.p.m. H₂O for the eclogites from the first and second core segment, respectively.

Profiles of average water contents in garnet from the eclogites, gneisses and garnet amphibolite as well as in omphacite from the eclogites are plotted in Figs 5 and 6 along with mineral $\delta^{18}\text{O}$ profiles for the two core segments. For the first core segment, most of the eclogites and gneisses have relatively homogeneous garnet water contents of 171–319 p.p.m. within analytical uncertainties. However, eclogite 02CCSD-II4A and gneiss 02CCSD-I2A far away from the boundary

between eclogite and gneiss have the highest water contents of 534–724 p.p.m. in garnet (Table 2; Fig. 5). Because garnet in the gneisses from the second core segment is rare and fine-grained, its water content could not be measured. Similarly, only one garnet grain was analysed for the garnet amphibolite.

Difficulties were also encountered in the analysis for water content of omphacite in the eclogites from the two core segments because of the variable retrograde metamorphism, so that only seven eclogite samples were analysed. Thus, water content variation with spatial distribution for garnet from the second core segment and for omphacite from the two core segments is not available. Nevertheless, the available data show that the garnet amphibolite and most of the eclogites from the second core segment have relatively homogeneous water contents of 301–392 p.p.m. in garnet, and the highest content of 548 p.p.m. is also observed in eclogite 02CCSD-II3A (Fig. 6). Omphacite in eclogites has water contents of 319–430 p.p.m. and 260–369 p.p.m. for the first and second core segments, respectively (Tables 2 & 3). It appears that there is a positive correlation of the water contents between garnet and omphacite for each sample (Figs 5 & 6) except sample 02CCSD-II4A.

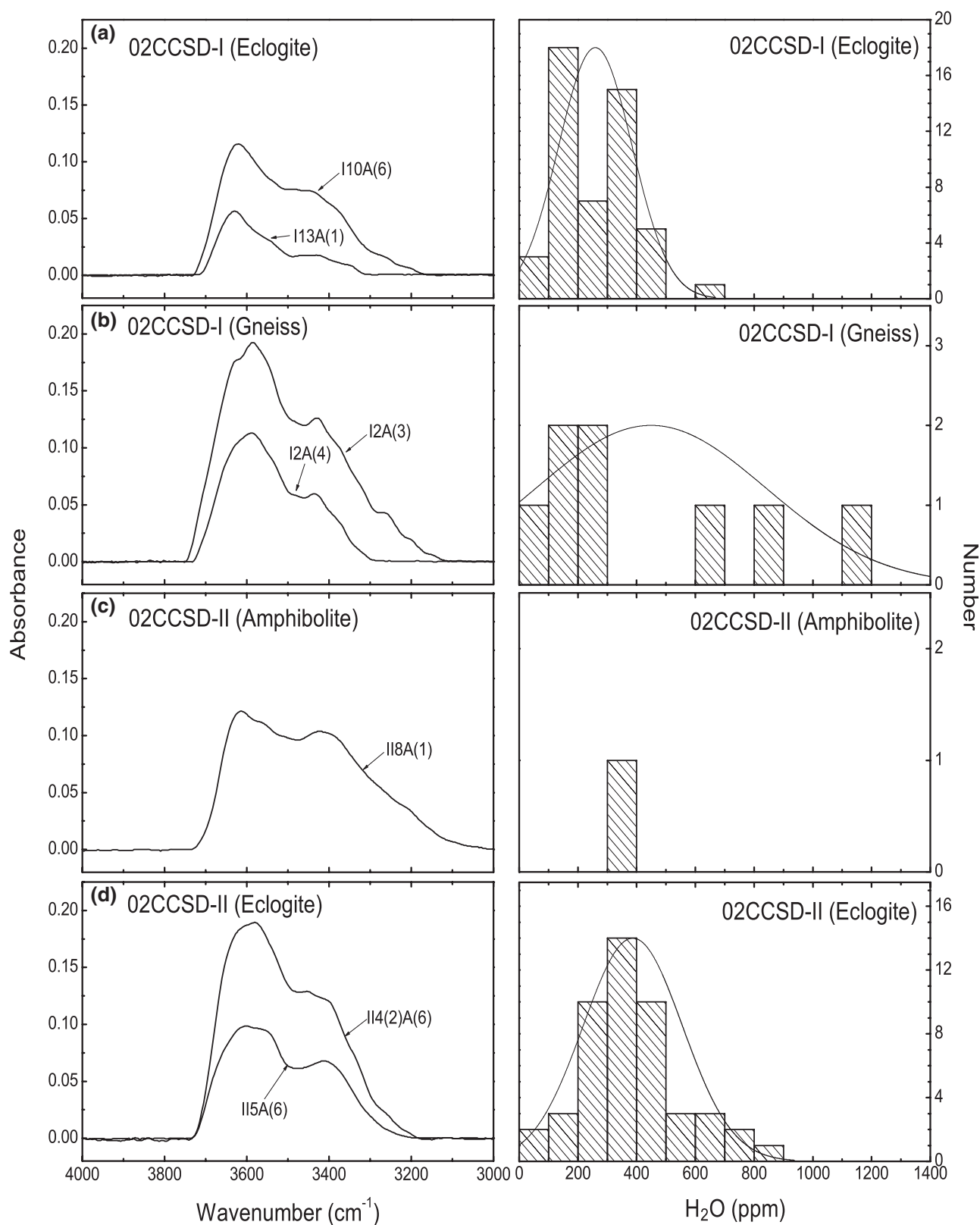


Fig. 7. Characteristic bands and hydroxyl content of garnet in different core segments of Chinese Continental Scientific Drilling main hole. The number in parenthesis after the sample number is the Fourier Transform Infrared Spectroscopy analysis number.

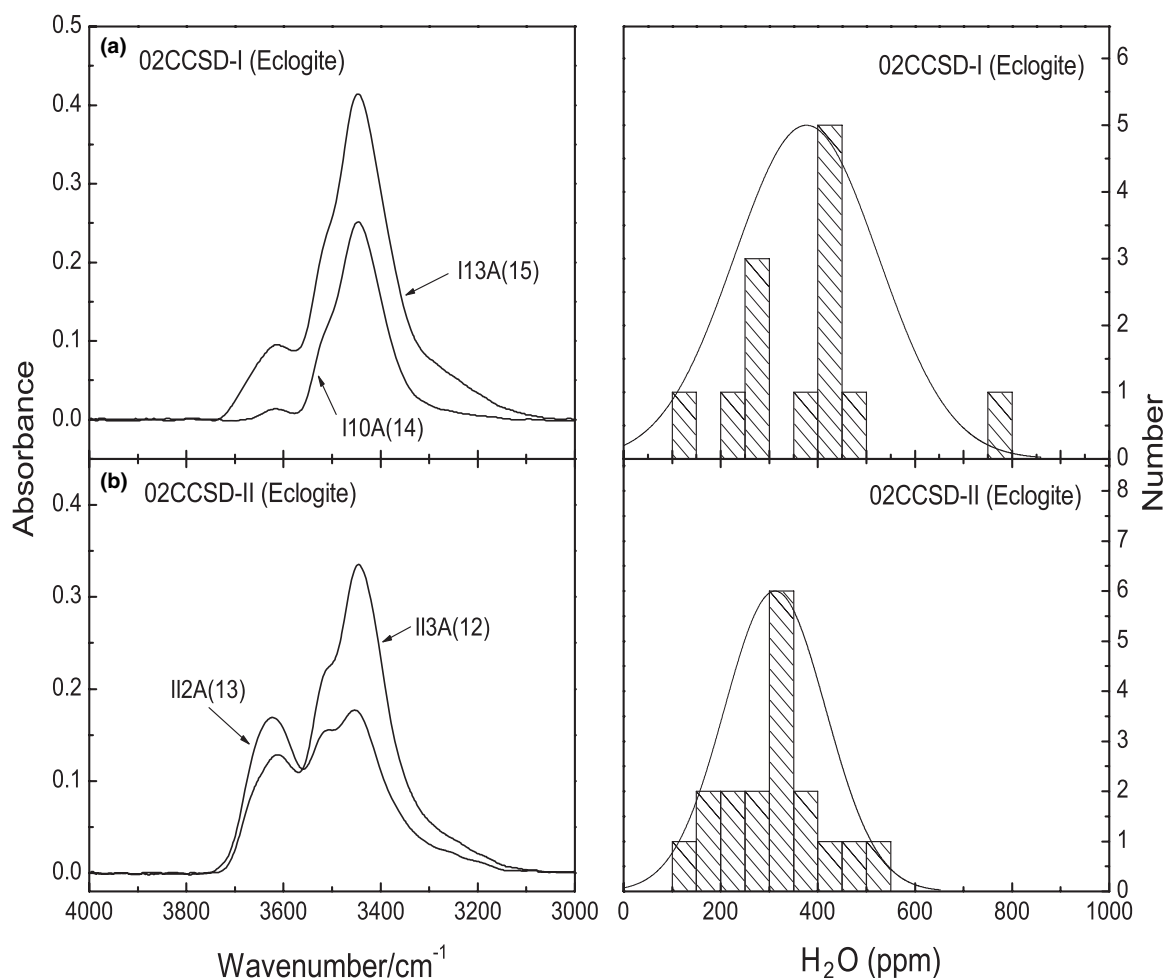


Fig. 8. Characteristic bands and hydroxyl content of omphacite in different core segments of Chinese Continental Scientific Drilling main hole. The number bracketed after the sample number is the Fourier Transform Infrared Spectroscopy analysis number.

DISCUSSION

^{18}O depletion in eclogite and gneiss

Metamorphic rocks have O isotope compositions that are usually similar to those of igneous and sedimentary rocks, with $\delta^{18}\text{O}$ values ranging from 6 to 18‰, depending on the geochemical nature of protolith and the degree of water–rock interaction during prograde metamorphism (e.g. Sharp *et al.*, 1993; Hoefs, 2004). A large variation in $\delta^{18}\text{O}$ from –11 to +10‰ has been observed in the UHP eclogites and associated gneisses from the surface outcrops along the Dabie–Sulu orogenic belt, with both equilibrium and disequilibrium fractionations of O isotope among coexisting minerals (Zheng *et al.*, 2003, and references therein). There is a consensus that the UHP rocks acquired their unusually negative $\delta^{18}\text{O}$ values down to –11‰ during high-*T* meteoric-hydrothermal alteration prior to the Triassic UHP metamorphism (Zheng *et al.*, 2003, and references therein). The water–rock interaction occurred in the middle Neoproterozoic, which resulted in large-scale

^{18}O -depletion of the protoliths of the UHP rocks along the northern margin of the South China Block, with an outcrop area of over 20 000 km² (Rumble *et al.*, 2002; Zheng *et al.*, 2003, 2004). The eclogites and gneisses in this study also show variable ^{18}O -depletion in the CCSD-MH core samples relative to the normal mantle-derived rocks (Table 1). The O isotope equilibrium fractionations between quartz and garnet have been preserved, yielding reasonable temperature estimates responsible for eclogite-facies metamorphic conditions (Fig. 4a). Therefore, the ^{18}O -depletion in the CCSD-MH eclogites and gneisses is also ascribed to the hydrothermal alteration of their protoliths by meteoric water at elevated temperatures before the continental subduction.

In the contact between eclogite and gneiss from the first core segment (Fig. 5), a gradual decrease occurs in the eclogite $\delta^{18}\text{O}$ when moving toward the gneiss but a gradual increase occurs in the gneiss $\delta^{18}\text{O}$ when moving toward the eclogite. In particular, positive O isotope fractionation between omphacite and garnet are retained not only for three samples of eclogite 02CCSD-I11A, -I12A and -I14A away from the eclogite–gneiss

Table 3. Fourier Transform Infrared Spectroscopy analysis of omphacite in ultrahigh-pressure eclogite from two Chinese Continental Scientific Drilling core segments.

Sample	Grain	Thickness (mm)	Band (cm ⁻¹)				Area (cm ⁻¹)	H ₂ O (p.p.m. wt)	Ave. H ₂ O (p.p.m. wt)
			I 3400–3450	II 3510–3550	III 3570–3600	IV 3610–3630			
02CCSD-I									
I10A	1	0.26	3447	3513	3616		64	476	430
	2		3447	3511	3622		52	387	
	3		3450	3509	3623		56	417	
	4		3448	3515	3618	3677	35	260	
	5		3450	3511	3618		39	290	
	6		3446	3513	3612		101	751	
I13A	1	0.35	3452		3607		51	284	335
	2		3440		3621		25	139	
	3		3440		3620		73	407	
	4		3445		3620		72	401	
	5		3448	3513	3615		80	445	
I14A	1	0.65	3445		3607		133	400	319
	2		3445	3515			79	237	
02CCSD-II									
II2A	1	0.30	3448	3511	3628		27	175	260
	2		3452	3508	3623		41	266	
	3		3455	3511	3625		52	338	
II3A	1	0.26	3447	3512	3628		32	242	369
	2		3447	3512	3613		70	530	
	3		3447	3511	3621		53	401	
	4		3447	3510	3630	3650	40	303	
II4(2)A	1	0.34	3443	3510	3620		70	396	296
	2		3446	3509	3620		28	158	
	3		3446	3509	3620		26	147	
	4		3442	3512	3621		86	487	
	5		3448	3507	3621		51	289	
II5A	1	0.31	3446	3509	3614		52	325	314
	2		3444	3511	3615		49	306	
	3		3443	3509	3614		51	319	
	4		3451	3509	3624		36	225	
	5		3451	3511	3611		50	312	
	6		3448	3511	3618		63	394	

boundary but also for three $\delta^{18}\text{O}$ -depleted samples of eclogite 02CCSD-I5A through -I7A close to the boundary. Such changes in the contact zone suggest either enhanced water–rock interaction during emplacement of gneissic protolith, or crustal contamination of the eclogitic protolith by ^{18}O -depleted gneissic protolith. The overall ^{18}O -depletion and heterogeneity for both eclogite and gneiss can be simply explained as resulting from interaction of their protoliths with meteoric water before subduction (Rumble & Yui, 1998; Zheng *et al.*, 1998, 2003). The differences in protolith $\delta^{18}\text{O}$ may have been caused by differences in the intensity of hydrothermal alteration controlled by water/rock ratio, temperature, proximity to permeable fracture zones, and the superposition of successive hydrothermal events (cf. Taylor, 1974, 1990).

For the second core segment, both eclogite and gneiss show a smaller variation in $\delta^{18}\text{O}$ but more ^{18}O -depletion compared with those from the first core segment (Figs 5 & 6). Once again, the preservation of eclogite–facies high- T O isotope fractionation between quartz and garnet suggests that the relatively pervasive water–rock interaction before subduction is responsible for the observed ^{18}O -depletion and homogeneous $\delta^{18}\text{O}$ distribution rather than the relatively widespread isotopic homogenization during amphibolite-facies retrogression. However, the considerable changes in

mineral $\delta^{18}\text{O}$ values at the contacts between eclogite, amphibolite and gneiss indicate that fluid-assisted O isotope exchange did take place at a local scale (less than ~ 0.5 m distance) during the amphibolite-facies retrogression.

More ^{18}O -depletion at the boundary between eclogite and gneiss suggests that the heterogeneous $\delta^{18}\text{O}$ distribution in the UHP rocks resulted from the meteoric-hydrothermal alteration of their protoliths triggered by magma emplacement. Preservation of the regular intensity signature of palaeo-hydrothermal circulation not only argues against regional isotope re-equilibration by the pervasive flow of metamorphic fluid, but also reinforces the case that the UHP complex, comprising eclogites and gneisses, retained large degree of structural coherence throughout continental subduction, UHP metamorphism and exhumation. This is consistent with the results of previous petrographic study. The common occurrence of coesite within zircon from both gneiss and eclogite from the MH of CCSD also points to *in situ* UHP metamorphism (Liu *et al.*, 2004a; Zhang *et al.*, 2006).

Effects of retrograde alteration

As shown in Fig. 3, the eclogites from the two core segments exhibit different degrees of retrograde meta-

morphism, and more abundant symplectites were observed in the transitions between eclogite and gneiss. This is especially obvious for the eclogites in the second core segment, as indicated by a transitional zone of garnet amphibolite between eclogite and gneiss. In the garnet amphibolite, most omphacite was retrograded to symplectite and there were few relict garnet, but amphibole and biotite are abundant (Fig. 3e). This indicates that the eclogite is significantly retrograded to garnet amphibolite or eclogitic gneiss at the contact zone between contrasting lithologies during exhumation due to a difference in fluid content (Zhang *et al.*, 2003). Previous petrographic studies also indicate that the eclogite and gneiss from CCSD-MH not only underwent the UHP metamorphism but also suffered amphibolite-facies retrogression during exhumation (e.g. Liu *et al.*, 2002; Su *et al.*, 2005; Zhang *et al.*, 2006). Isotopic exchange between minerals and retrograde fluid is expected during exhumation, and may result in isotopic disequilibrium among minerals and/or the lower O isotope temperatures of mineral pairs than the UHP metamorphic conditions.

Eclogite-facies temperatures are indicated by the quartz–garnet pair O isotope fractionations, which yield 575–770 °C for the eclogite and 560–730 °C for the gneiss (Fig. 4; Table 1). On the other hand, the O isotope temperatures for the other minerals are differentially lower than the temperatures of the eclogite-facies metamorphism when paired with quartz, suggesting retrograde isotope exchange subsequent to the eclogite-facies metamorphism. The range in isotope temperatures for the different mineral pairs is interpreted to have been caused by differential isotope exchange between minerals and retrograde fluid during exhumation. Minerals such as omphacite, muscovite, biotite, rutile, epidote and feldspar have fast rates of O diffusion (Zheng & Fu, 1998), and thus are susceptible to retrograde isotope exchange with water. In contrast, garnet has slow rates of O diffusion and is resistant to O isotope exchange (Zheng & Fu, 1998), giving the best estimate for the peak metamorphic temperatures when paired with quartz (e.g. Rumble & Yui, 1998; Zheng *et al.*, 1998, 1999). Differential exchange of H and O isotopes with retrograde fluid during exhumation has also been observed in some of the UHP eclogite minerals from surface outcrops along the Dabie–Sulu orogenic belt (Baker *et al.*, 1997; Rumble & Yui, 1998; Zheng *et al.*, 1998, 1999, 2002; Fu *et al.*, 1999; Xiao *et al.*, 2002; Zhang *et al.*, 2003).

O isotope disequilibrium between omphacite and garnet has also been found for some of the eclogites from the two core segments in this study (Fig. 9). The O isotope fractionation between omphacite and garnet in the eclogites can be classified into the three types: (1) negative and zero fractionations of -0.5 to 0‰ , which clearly indicate isotopic disequilibrium and yield unreasonably lower isotopic temperatures of 380–585 °C calculated from quartz–omphacite pairs (Table 1); (2) positive fractionation of 1.5‰ , which is

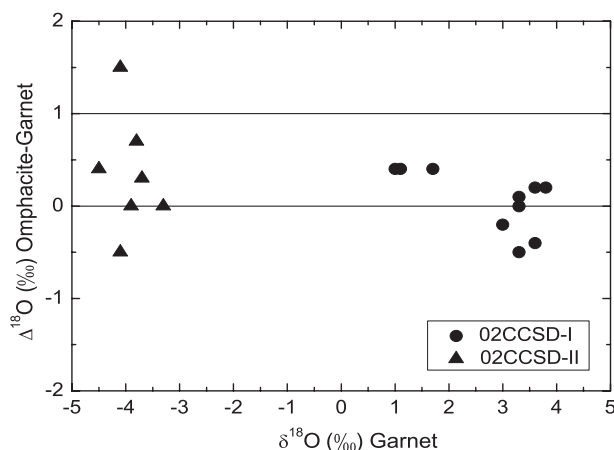


Fig. 9. O isotope fractionations between omphacite and garnet v. the $\delta^{18}\text{O}$ values of garnet from the two core segments of Chinese Continental Scientific Drilling main hole. The reference lines of $\Delta = 0\text{‰}$ and 1‰ place the approximate limit of equilibrium fractionations between omphacite and garnet, whereas the samples beyond the two lines are out of isotopic equilibrium.

out of isotopic equilibrium at eclogite-facies temperatures; (3) positive fractionations of 0.1 – 0.7‰ which are at isotopic equilibrium.

As pointed out by Zheng *et al.* (2003), one of the following processes can cause O isotopic disequilibrium between omphacite and garnet: (1) the inheritance of magmatic minerals during metamorphism, for instance, incomplete metamorphic reaction from gabbro to eclogite; (2) the presence of accessory mineral inclusions in omphacite and/or garnet; (3) retrograde alteration, for instance, the symplectitic replacement of omphacite and differential isotopic exchange with retrograde fluid. Where symplectites and retrograde minerals such as amphibole and biotite occur in some of the eclogites (Fig. 3), the O isotope disequilibrium is obviously caused by retrograde alteration. It appears that the state of equilibrium or disequilibrium O isotope fractionation between omphacite and garnet is correlated with variation in their water content at local scales. For example, omphacite water contents for the eclogites 02CCSD-I14A, -I13A and -I10A from the first core segment increase from 319 p.p.m. to 335–430 p.p.m., the O isotope fractionation between omphacite and garnet change from equilibrium for sample 02CCSD-I14A to disequilibrium for samples 02CCSD-I13A and I10A (Fig. 5). A change in omphacite-garnet fractionation from a positive equilibrium value in eclogite 02CCSD-I14A to a negative disequilibrium value in eclogite 02CCSD-I13A corresponds to a decrease in garnet water content from 534 to 200 p.p.m. (Table 2). In contrast, a change in garnet-epidote fractionation from a positive equilibrium value in gneiss 02CCSD-I3A to a negative disequilibrium value in gneiss 02CCSD-I2A corresponds to an increase in garnet water content from 171 to 724 p.p.m. (Table 2). In both cases, disequilibrium is

associated with the large changes in mineral water content.

For the second core segment, the O isotope fractionation between omphacite and garnet changes from a positive equilibrium value at eclogite 02CCSD-II4(2)A to a negative disequilibrium value at eclogite II5A close to the eclogite–amphibolite boundary (Fig. 6), suggesting the effect of retrograde alteration of omphacite. Disequilibrium fractionations in eclogites 02CCSD-II3A and -II4(1)A correspond to a significant increase in the water content of both omphacite and garnet from eclogite 02CCSD-II2A to -II3A, indicating the correlation between the retrograde disequilibrium and the water incorporation into the eclogite minerals. Increases in quartz and feldspar $\delta^{18}\text{O}$ values also occur at the gneiss–amphibolite boundary, but no measurement of water content in these minerals is available for comparison. In order to establish reasonable correlations between the equilibrium/disequilibrium state and the mineral water content, many more measurements of water content in nominally anhydrous minerals are needed.

Previous studies of petrography and stable isotopes reveal that retrograde metamorphism is widespread in the UHP eclogites from the surface outcrops in the Dabie–Sulu orogenic belt, and the common retrograde reactions include symplectitic replacement of omphacite, biotite + plagioclase replacement of phengite, and the formation of edenitic/pargasitic amphibole (e.g. Wang & Liou, 1991; Cong *et al.*, 1995; Yui *et al.*, 1997; Zheng *et al.*, 1999, 2002; Zhang *et al.*, 2000, 2003). Fluid infiltration to drive hydration is indicated by abundant fluid inclusions in post-peak metamorphic minerals and by the occurrence of OH-bearing minerals (such as amphibole and layer silicates). The O isotopic composition of less resistant minerals provides a useful constraint on the origin of retrograde fluid. O isotope geothermometers of quartz–mineral pairs (e.g. feldspar, muscovite, epidote, biotite and rutile) give temperatures compatible with amphibolite-facies conditions (Fig. 4), suggesting the retrograde minerals could approach and preserve O isotope re-equilibration under the amphibolite-facies conditions.

Retrograde reactions of eclogite to amphibolite commonly take place during exhumation due to the infiltration of externally derived fluids along fault zones or lithological layers; however, both refractory and retrograde minerals paired with quartz show approximately linear $\delta^{18}\text{O}$ variations (Fig. 4). These fall within the framework of their protolith's O isotope heterogeneity, and thus there is no significant O isotope shift during retrograde metamorphism. This suggests that the retrograde fluid was either in, or very close to, isotopic equilibrium with the minerals from the UHP metamorphic rocks (Zheng *et al.*, 1999). In other words, the retrograde fluids were internally buffered in their stable isotope compositions; local isotope composition depends on precursor composition and thus has generally inherited the nature of

premetamorphic protolith that experienced meteoric–hydrothermal alteration at high temperatures (Zheng *et al.*, 1999, 2002, 2003, 2004; Zhang *et al.*, 2003).

Zheng *et al.* (2003) postulated that retrograde fluid originates from the decomposition of hydrous minerals, the decrepitation of primary fluid inclusions, and the exsolution of structural hydroxyl of nominally anhydrous minerals. Minor OH-bearing minerals such as phengite, zoisite/epidote, glaucophane and talc have been observed to occur as matrix minerals or as inclusions in some of UHP metamorphic rocks from the Dabie–Sulu orogenic belt (e.g. Liou *et al.*, 1995; Nagasaki & Enami, 1998; Zhang *et al.*, 2002), implying that they are metastable at UHP conditions and thus can store significant amounts of H_2O from premetamorphic protoliths at mantle depths. In the process of UHP slab exhumation, the hydrous minerals should decompose to provide considerable amounts of retrograde fluid. Intensive studies of fluid inclusions in the UHP eclogites from the Dabie–Sulu orogenic belt show the preservation of prograde and peak metamorphic fluids despite significant disturbance during exhumation (e.g. Xiao *et al.*, 2000, 2001, 2002; Fu *et al.*, 2001, 2002, 2003a,b; Su *et al.*, 2002). An abrupt decrease in pressure is expected to cause decrepitation of fluid inclusions, producing small amounts of retrograde fluid.

Using hydroxyl concentrations in clinopyroxene from mantle eclogite xenoliths in South African kimberlites, Smyth *et al.* (1991) proposed that re-equilibration of pyroxene during cooling from crystallization temperature to their observed equilibration conditions (~ 1050 – 1250 °C in the 3–5 GPa range) could evolve sufficient hydroxyl. This possibility was used to explain extensive occurrence of such hydrous phases as amphibole and phlogopite in the eclogite xenoliths, with the expectation that a small amount of partial melt would result at depths of ~ 100 km. Retrograde breakdown of omphacite in HP eclogites in Italian Western Alps was envisaged to be kinetically triggered by the fluid inclusions that formed by low-pressure re-equilibration of a fluid presumably trapped at eclogite facies conditions (Vallis & Scambelluri, 1996). Hydroxyl exsolution from pyroxene during decompression was conceived by Philippot & Scambelluri (1996) to represent an alternative source for the analysed inclusions. On the other hand, core clusters of aqueous inclusions in HP pyroxene pseudomorphing igneous augite in Alpine eclogites were suggested to have a connection with prograde breakdown of pre-eclogitic hydrous phases (Nadeau *et al.*, 1993).

With the subduction of continental crust into mantle depths, water could be incorporated as OH^- not only into hydroxyl-bearing minerals (e.g. phengite), but also into nominally anhydrous minerals (e.g. omphacite, garnet and rutile) together with molecular H_2O . Decompression exsolution of structural hydroxyl from nominally anhydrous minerals in UHP rocks can form

an important source of retrograde fluid (Zheng *et al.*, 1999). As argued by Zheng *et al.* (2003), this hypothesis has gained more and more support not only from the measurement of hydroxyl content in nominally anhydrous minerals from UHP eclogites, but also from the experimental determination of hydroxyl solubility in the minerals.

Previous FTIR studies on nominally anhydrous minerals in the UHP eclogites from the Dabie–Sulu orogenic belt show that they contain significant amounts of hydroxyl, with 115–1300 p.p.m. H₂O (by weight) in omphacite, 92–1735 p.p.m. H₂O in garnet, and 4300–9600 p.p.m. H₂O in rutile (Zhang *et al.*, 2001, 2004; Xia *et al.*, 2005). The present study also shows that garnet contains 50–776 p.p.m. H₂O and 96–1144 p.p.m. H₂O for the eclogites and the gneisses, respectively; omphacite in the eclogites has 139–751 p.p.m. H₂O (Tables 2 & 3; Figs 7 & 8).

A number of experimental investigations have shown that hydroxyl solubility in nominally anhydrous minerals decreases with decreasing pressure (Lu & Keppler, 1997; Withers *et al.*, 1998; Mosenfelder, 2000; Rauch & Keppler, 2002; Koch-Müller *et al.*, 2003; Bromiley *et al.*, 2004a,b; Mierdel & Keppler, 2004). A linear increase in the water content of omphacite and garnet with pressure is observed from the Kokchetav eclogite (Katayama *et al.*, 2006). It is to be expected that solubility of hydroxyl in the nominally anhydrous minerals decreases rapidly with abruptly decreasing pressure in the early stage of UHP slab exhumation, resulting in release of the significant amounts of aqueous fluid (Zheng *et al.*, 1999, 2003). In this regard, many nominally anhydrous minerals have lost a significant part of their original water during decompression associated with exhumation. Therefore, the amount of measured structural hydroxyl only provides a minimum estimate of dissolved water at mantle depths. Structural hydroxyl in hydroxyl-bearing silicates is depleted in ¹⁸O relative to the framework of anhydrous silicate (Zheng, 1993b), and it is reasonable to assume that the structural hydroxyl within the nominally anhydrous minerals is considerably depleted in ¹⁸O with respect to the host minerals. Thus, the accumulation of hydroxyl liberated from nominally anhydrous minerals can form an important source of the low $\delta^{18}\text{O}$ retrograde fluid, resulting in the negative O isotope disequilibrium fractionation between omphacite and garnet in some of eclogites (Fig. 9) and the lower isotopic temperatures obtained by the retrograde minerals when paired with quartz (Table 1; Fig. 4).

For jadeite from jadeite quartzite in the Dabie orogen, Su *et al.* (2004) observed high concentrations of hydroxyl in cores (1200–3894 p.p.m. H₂O by weight) but low concentrations of hydroxyl in mantles and rims (212–1422 p.p.m. H₂O). Because hydroxyl solubility in jadeite increases with decreasing pressure at 2–10 GPa (Bromiley & Keppler, 2004), the effect of

hydroxyl exsolution by decompression cannot simply be applied to this interesting observation. A number of factors may control such a reversed behaviour, including the incorporation modes of hydroxyl into jadeite, the presence or absence of lower valence cations on the M1 site, the number of M2 vacancies in the mineral structure, the substitution of Na by OH, and the bulk composition of solid solution between jadeite and omphacite. Probably, a change in mechanisms for hydroxyl incorporation into jadeite may occur in response to the pressure change during its formation and recrystallization in the processes of subduction and exhumation.

Quantitative estimates of water loss from minerals during exhumation

Due to the decompression effect, many nominally anhydrous minerals have lost significant amounts of their original water during exhumation. In order to estimate the amount of water lost from eclogite by decompression exsolution of structural hydroxyl, it is necessary to know the initial water content prior to dehydration, the remaining water content subsequent to dehydration and the densities of garnet and omphacite in UHP eclogites. The parameters used in the present calculations were determined in the following ways.

Initial water content

Structural hydroxyl content in garnet from the Dabie–Sulu orogenic belt ranges from 92 to 1735 p.p.m. H₂O (by weight), but most are between 200 and 1000 p.p.m. (Zhang *et al.*, 2004; Xia *et al.*, 2005; this study). Similarly, garnet from Kazakhstan has hydroxyl contents of 10–2500 p.p.m. H₂O, with a cluster between 200 and 800 p.p.m. (Langer *et al.*, 1993; Katayama *et al.*, 2006). We assume an initial water content of 800 p.p.m. for garnet. Omphacite from eclogite in the Dabie–Sulu orogenic belt has hydroxyl contents of 115–1300 p.p.m. H₂O (Zhang *et al.*, 2001, 2004; this study); those from Kazakhstan have 1030–3020 p.p.m. H₂O, mostly ~1000 p.p.m. (Katayama & Nakashima, 2003). Thus, 1000 p.p.m. was used as the initial water content for omphacite.

Remaining water content

The garnet in the eclogites from the two core segments of CCSD-MH has structural hydroxyl contents of 50–841 p.p.m. (Table 2), but most are between 200 and 500 p.p.m. with an average of ~320 p.p.m. A H₂O content of 300 p.p.m. was assumed as the remaining water content for garnet. The omphacite has structural hydroxyl contents of 139–751 p.p.m. (Table 3), but most of them are between 200 and 500 p.p.m. with an average of ~340 p.p.m. Hence, 400 p.p.m. was taken as the remaining water content for omphacite.

Mineral density

As garnet and omphacite are solid solutions, it is necessary to know the chemical composition of the CCSD-MH samples in order to estimate density. Mineral chemistry analysis was made by Wang *et al.* (1995) for eclogites at Mengzhong where the CCSD-MH is located. The results show 27–50% pyrope, 32–39% grossular, 20–42% almandine for garnet. We assume that the garnet from the two core segments has a composition of 35% pyrope, 35% grossular, and 30% almandine. The densities for the three end-members of garnet are 3.56 g cm^{-3} for pyrope, 3.60 g cm^{-3} for grossular, and 4.31 g cm^{-3} for almandine. As a result, a density of 3.80 g cm^{-3} for garnet was obtained by weighted mean. As estimated by Wang *et al.* (1995), omphacite in the eclogites at Mengzhong contains jadeite (30–58%), augite (0–13%), and aegirine (44–54%) components. Omphacite is used with a composition of 45% jadeite, 5% diopside and 50% aegirine for the calculations. The densities of jadeite, diopside and aegirine are 3.34 , 3.28 and 3.58 g cm^{-3} , respectively and a density of 3.46 g cm^{-3} for omphacite was obtained by weighted mean.

We have calculated how much water can be released from eclogites for a hand specimen ($3 \times 6 \times 9 \text{ cm}$) and a lensoid outcrop ($10 \times 5 \times 20 \text{ m}$) with variable composition using the densities given above (Table 4). The decompression exsolution of structural hydroxyl from a hand specimen and lens of eclogite can release 0.051–0.059 wt% H_2O (0.311–0.333 g and 1917.60–2058.40 kg, respectively, for the two cases). If these amounts of released water were

consumed to generate amphibole, the amount of hornblende that could form in the eclogites can be calculated by taking the water content of amphibole. According to the chemical formula of different amphibole, their H_2O contents vary from ~1.8% to 2.2% for tremolite-actinolite, from ~1.8% to 2.2% for hornblende and from ~1.9% to 2.3% for glaucophane. It is assumed that amphibole has a water content of 2.2% by weight (e.g. Schmidt & Poli, 2003).

A hand specimen of eclogite composed of 70% garnet and 30% omphacite can release 0.316 g water to form 14.4 g amphibole during exhumation (Table 4). The eclogite lens of the same composition can deliver 1952.80 kg water to form 88763.64 kg amphibole. Beside garnet and omphacite, eclogite also contains minor amounts of hydroxyl-bearing minerals (e.g. phengite $\pm$ epidote) and the other nominally anhydrous minerals (e.g. rutile $\pm$ kyanite $\pm$ quartz). They can also dehydrate significantly during exhumation; therefore, the present estimates only provide the minimum amount of the water that was actually lost from the eclogites during exhumation.

Felsic gneiss contains a considerable amount of hydroxyl-bearing minerals (e.g. mica $\pm$ epidote) and nominally anhydrous minerals (e.g. feldspar + quartz $\pm$ magnetite), which contain structural hydroxyl and molecular H_2O (Gong *et al.*, 2007). Gneiss stores much more water than the eclogite under the same UHP conditions, thus the gneiss can release more water than eclogite during exhumation of deeply subducted slabs. We envisage that the released water would flow from the gneiss to the eclogite to cause the remarkable hydration of the eclogite adjacent to the gneiss.

Table 4. Estimate of water amounts by hydroxyl exsolution from eclogite during exhumation.

Garnet (vol.%)	Omphacite (vol.%)	Rock weight (kg)	Initial H ₂ O weight (kg)			Remaining H ₂ O weight (kg)			H ₂ O loss (kg)	Hornblende (kg)	WR H ₂ O content (wt%)			
			Garnet	Omphacite	Whole rock	Garnet	Omphacite	Whole rock			Before	After	Loss	
3 × 6 × 9 cm														
10	90	0.566	4.92 × 10 ⁻⁵	5.04 × 10 ⁻⁴	5.54 × 10 ⁻⁴	1.85 × 10 ⁻⁵	2.02 × 10 ⁻⁴	2.20 × 10 ⁻⁴	3.33 × 10 ⁻⁴	0.0152	0.098	0.039	0.059	
20	80	0.572	9.85 × 10 ⁻⁵	4.48 × 10 ⁻⁴	5.47 × 10 ⁻⁴	3.69 × 10 ⁻⁵	1.79 × 10 ⁻⁴	2.16 × 10 ⁻⁴	3.31 × 10 ⁻⁴	0.0150	0.096	0.038	0.058	
30	70	0.577	1.48 × 10 ⁻⁴	3.92 × 10 ⁻⁴	5.40 × 10 ⁻⁴	5.54 × 10 ⁻⁵	1.57 × 10 ⁻⁴	2.12 × 10 ⁻⁴	3.28 × 10 ⁻⁴	0.0149	0.094	0.037	0.057	
40	60	0.583	1.97 × 10 ⁻⁴	3.36 × 10 ⁻⁴	5.33 × 10 ⁻⁴	7.39 × 10 ⁻⁵	1.35 × 10 ⁻⁴	2.08 × 10 ⁻⁴	3.25 × 10 ⁻⁴	0.0148	0.092	0.036	0.056	
50	50	0.588	2.46 × 10 ⁻⁴	2.80 × 10 ⁻⁴	5.27 × 10 ⁻⁴	9.23 × 10 ⁻⁵	1.12 × 10 ⁻⁴	2.04 × 10 ⁻⁴	3.22 × 10 ⁻⁴	0.0146	0.090	0.035	0.055	
60	40	0.594	2.95 × 10 ⁻⁴	2.24 × 10 ⁻⁴	5.20 × 10 ⁻⁴	1.11 × 10 ⁻⁴	8.97 × 10 ⁻⁵	2.00 × 10 ⁻⁴	3.19 × 10 ⁻⁴	0.0145	0.088	0.034	0.054	
70	30	0.599	3.45 × 10 ⁻⁴	1.68 × 10 ⁻⁴	5.13 × 10 ⁻⁴	1.29 × 10 ⁻⁴	6.73 × 10 ⁻⁵	1.97 × 10 ⁻⁴	3.16 × 10 ⁻⁴	0.0144	0.086	0.033	0.053	
80	20	0.605	3.94 × 10 ⁻⁴	1.12 × 10 ⁻⁴	5.06 × 10 ⁻⁴	1.48 × 10 ⁻⁴	4.48 × 10 ⁻⁵	1.93 × 10 ⁻⁴	3.14 × 10 ⁻⁴	0.0143	0.084	0.032	0.052	
90	10	0.610	4.43 × 10 ⁻⁴	5.61 × 10 ⁻⁵	4.99 × 10 ⁻⁴	1.66 × 10 ⁻⁴	2.24 × 10 ⁻⁵	1.89 × 10 ⁻⁴	3.11 × 10 ⁻⁴	0.0141	0.082	0.031	0.051	
10 × 5 × 20 m														
10	90	3 494 000	304.00	3114.00	3418.00	114.00	1245.60	1359.60	2058.40	93563.64	0.098	0.039	0.059	
20	80	3 528 000	608.00	2768.00	3376.00	228.00	1107.20	1335.20	2040.80	92763.64	0.096	0.038	0.058	
30	70	3 562 000	912.00	2422.00	3334.00	342.00	968.80	1310.80	2023.20	91963.64	0.094	0.037	0.057	
40	60	3 596 000	1216.00	2076.00	3292.00	456.00	830.40	1286.40	2005.60	91163.64	0.092	0.036	0.056	
50	50	3 630 000	1520.00	1730.00	3250.00	570.00	692.00	1262.00	1988.00	90363.64	0.090	0.035	0.055	
60	40	3 664 000	1824.00	1384.00	3208.00	684.00	553.60	1237.60	1970.40	89563.64	0.088	0.034	0.054	
70	30	3 698 000	2128.00	1038.00	3166.00	798.00	415.20	1213.20	1952.80	88763.64	0.086	0.033	0.053	
80	20	3 732 000	2432.00	692.00	3124.00	912.00	276.80	1188.80	1935.20	87963.64	0.084	0.032	0.052	
90	10	3 766 000	2736.00	346.00	3082.00	1026.00	138.40	1164.40	1917.60	87163.64	0.082	0.031	0.051	

The calculations assume the initial hydroxyl contents of 800 p.p.m. H_2O wt for garnet and 1000 p.p.m. H_2O wt for omphacite, and the remaining hydroxyl contents of 300 p.p.m. H_2O wt for garnet and 400 p.p.m. H_2O wt for omphacite. Mineral end-member compositions were used to calculate average densities, yielding 3.80 g cm^{-3} for garnet and 3.46 g cm^{-3} for omphacite. Amphibole is assumed to have a water content of 2.2% by weight. The lost H_2O amounts for whole rock (WR) are calculated from the two cases before and after dehydration.

SUMMARY

Changes in mineral O isotope and hydroxyl content across the boundary between eclogite and gneiss are studied in detail in the CCSD-MH cores. As a result, both the origin and mobility of metamorphic fluid during exhumation are deciphered.

Mineral separates from the contact between UHP eclogite and gneiss show considerable changes in oxygen isotope ratios for two core segments at 734.21–737.16 and 929.67–932.86 m. Considerable changes in mineral $\delta^{18}\text{O}$ values occur at the eclogite–amphibolite–gneiss boundaries, indicating that fluid-assisted O isotope exchange did take place at a local scale (less than ~ 0.5 m distance) during the amphibolite-facies retrogression. Eclogites have $\delta^{18}\text{O}$ values of -4.5 to 3.8‰ for garnet and -4.6 to 4.0‰ for omphacite; gneisses have $\delta^{18}\text{O}$ values of -0.4 to 2.4‰ for quartz, -2.0 to 0.8‰ for feldspar and -3.8 to -1.9‰ for garnet. Both equilibrium and disequilibrium O isotope fractionation were observed between quartz and the other minerals, with reversed fractionation between omphacite and garnet in some of eclogite samples. Preservation of O isotope equilibrium between quartz and garnet at eclogite-facies metamorphic temperatures indicates that eclogite and gneiss protoliths acquired the low $\delta^{18}\text{O}$ values by meteoric water–rock interaction at high temperatures before subduction. Heterogeneous $\delta^{18}\text{O}$ distribution is observed for the eclogites and gneisses from the first core segment, which is ascribed to differences in their protoliths $\delta^{18}\text{O}$ that may have been caused by differences in the intensity of original hydrothermal alteration.

Garnet from the eclogites and gneisses and omphacite from the eclogites contain significant amounts of water occurring as structural hydroxyl. FTIR analyses gave H_2O concentrations of 50–1144 p.p.m. (by weight) for garnet, and 139–751 p.p.m. for omphacite. This has only provided the lower limit of dissolved hydroxyl in the nominally anhydrous UHP minerals at mantle depths because the large fractions of structural water have escaped upon decompression. The state of equilibrium or disequilibrium O isotope fractionations between omphacite and garnet is correlated with variation in their water content at local scales, indicating that the internally derived fluid plays a critical role in the retrograde metamorphism during exhumation. Retrograde metamorphism results in O isotope disequilibria between some of the minerals and mineral reactions, but the fluid for retrograde reactions was derived from the decompression exsolution of structural hydroxyl and thus internally buffered in the O isotope compositions. A quantitative estimate suggests that a hand specimen ($3 \times 6 \times 9$ cm) of eclogite composed of 70% garnet and 30% omphacite can release 0.316 g water by the decompression exsolution of structural hydroxyl, which can form 14.4 g amphibole during exhumation. This provides sufficient amounts of water for amphibolite-facies retrogression.

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