

Water contents and hydrogen isotopes in nominally anhydrous minerals from UHP metamorphic rocks in the Dabie-Sulu orogenic belt

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A continuous flow method, by a combination of thermal conversion elemental analyzer (TC/EA) with isotope ratio mass spectrometry (MS), was developed to determine both H isotope composition and H₂O concentration of ultrahigh-pressure (UHP) metamorphic rocks in the Dabie-Sulu orogenic belt. By using the developed step-heating technique, we have studied H₂O concentration and H isotope composition of the different forms of water (structural OH and molecular H₂O) in garnet. The quantitative measurements of H₂O concentration and H isotope composition of minerals in UHP metamorphic rocks from several typical outcrops indicate that the gneisses can release more amounts of water than the eclogites during exhumation of the deeply subducted continental crust. Therefore, by decompression dehydration at the contact between eclogite and gneiss, the released water could flow from the gneiss to the eclogite and result in significant hydration of the eclogite adjacent to the gneiss. The measured maximum water contents of minerals in eclogites indicate that garnet and omphacite have the maximum water solubilities of 2500 and 3500 ppm, respectively, under the peak UHP metamorphic conditions.

eclogite, gneiss, mineral, structural hydroxyl, molecular water, metamorphic fluid

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Water occurs as modal and cryptic components in high-pressure (HP) and ultrahigh-high pressure (UHP) metamorphic rocks [1]. As a modal component, water is present as hydrous minerals such as phengite, epidote and lawsonite in the deeply subducted continental crust. Their stability during subduction and exhumation of continental crust is a key to the flow of metamorphic aqueous fluid under HP to UHP conditions [2]. As a cryptic component, water is present as structural hydroxyl and molecular water in nominally anhydrous minerals (NAMs). Despite their low abundances, these cryptical components form an important reservoir of water in UHP metamorphic slices [3]. Considerable amounts of fluid inclusion have been observed to occur in quartz, garnet, omphacite, kyanite, epidote and zircon in

the UHP metamorphic rocks from the Dabie-Sulu orogeny [4,5]. Both transmission electron microscope (TEM) and Fourier transform IR spectroscopy (FTIR) analyses have detected clusters of water in the form of molecular H₂O in garnet, omphacite, jadeite and quartz in the UHP metamorphic rocks from the Dabie-Sulu orogeny [6,7]. Therefore, molecular H₂O, which is an assignable form of water, occurs as macro- to nano-scale fluid inclusions and water clusters in minerals [8,9].

The determination of both H isotope compositions and H₂O concentrations of different forms of water in minerals provides a power tool to study fluid regime and its geochemical effect during continental subduction and exhumation [10,11]. The measurement of water concentration has been one of the forefront subjects in deep Earth science [12]. Special attention has been paid to the concentration of

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structural hydroxyl in NAMs from UHP metamorphic eclogite [13–19]. For the origin of retrograde fluid, only stable isotope can provide the most useful constraints [20,21]. Therefore, we have developed an online continuous flow method, combining a thermal conversion elemental analyzer (TC/EA) with isotope ratio mass spectrometry (MS) for determination of both H isotope composition and H₂O concentration of minerals. By using the TC/EA-MS online technique, we have made systematic analyses of both H isotope composition and H₂O concentration of minerals in the UHP metamorphic rocks from several typical outcrops in the Dabie-Sulu orogen and core samples of the Chinese Continental Scientific Drilling (CCSD) project. In combination with O isotope analysis by the laser fluorination (LF) technique, the results provide important geochemical constraints on fluid regime during continental subduction-zone metamorphism.

1 Analytical methods

The on-line TC/EA-MS continuous flow method is not only capable of determining the H₂O concentration but also suitable for analyzing the H isotope composition of hydrous minerals and NAMs [22]. Our protocols show that the routine analysis of sample sizes is as small as 0.01 μ L H₂O for both H isotope composition and H₂O concentration in hydrous and nominally anhydrous minerals. The measured H isotope ratios are presented in the conventional δD notation relative to VSMOW, and the water contents are presented in H₂O ppm by weight. Hydrogen concentration of 5.0 wt% for benzoic acid (C₇H₆O₂) is used to be a standard for H₂O concentration analysis, and its absolute reproducibility is better than $\pm 0.05\%$ (1σ). A δD value for biotite NBS-30 is fixed at -65.7% for correction to instrumental fractionations during the routinely H isotopic analysis. The average reproducibility for the δD value is better than $\pm 1.0\%$. Bulk analytical errors appear to depend on mineral water contents. In practice, the analytical errors for the δD value and H₂O content can be as small as $\pm 0.5\%$ (1σ) and $\pm 1\%$ (1σ) for hydrous minerals, respectively. Because of the low water content in the NAMs, a home-standard garnet 04BXL02 which has a δD value of $-93\pm 2\%$ and a total H₂O content of 520 ± 16 ppm by weight was used in the analyses of NAMs [11]. The analytical errors for the δD value and the H₂O content can be generally about $\pm 2\%$ (1σ) and $\pm 5\%$ (1σ) for NAMs, respectively. Both precision and accuracy of the TC/EA-MS method are comparable to the conventional manometric methods. Therefore, the TC/EA-MS technique is a useful tool to quantitatively determine the both H₂O concentration and H isotope composition of hydrous and nominally anhydrous minerals.

The direct analysis by TC/EA-MS method can only determine the content and H isotope composition of total water in the minerals. In order to distinguish structural OH

from molecular H₂O in the NAMs, we have developed a stepwise-heating approach to extract the different forms of water from the NAMs for the TC/EA-MS analysis. Under the different temperatures of heating, the different forms of water can be released from minerals [11]. The results revealed that garnet grain of 50 μ m size which was heated at 350°C for 4 h also yielded constant δD values of $-86\pm 6\%$ and H₂O contents of 281 ± 13 ppm. The result for the H₂O contents agrees with H₂O contents of 271 ± 58 ppm measured by FTIR for the quantitative analysis of structural hydroxyl in the same garnet. This indicates that the procedure of heating garnet sample at 350°C for 4 hours has removed the molecular H₂O without loss of structural OH. Therefore, the δD values of $-86\pm 6\%$ for garnet heated at 350°C for 4 hours represent the H isotope composition of structural OH in the garnet. In this regard, the molecular H₂O is depleted in D relative to the structural OH in the garnet, implying much faster diffusion rates of molecular H₂O than the structural OH. Calculation by using H diffusion coefficient and diffusion equation suggests that the influence of H diffusion in the stepwise-heating approach and TC/EA-MS analyses can be precluded.

2 H₂O content and H isotope composition of minerals in eclogite at Bixiling

By using stepwise-heating TC/EA-MS method, we have measured water contents and H isotope compositions for the different forms of water in eclogite at Bixiling in the Dabie orogen (Figure 1). As shown in Figure 1, the molecular H₂O is much lower but smaller variation in content than the structural OH. For the H isotope composition, the molecular H₂O is depleted in D relative to the structural OH; the δD values of molecular H₂O show larger variation than the structural OH, indicating the variable origins of molecular H₂O. The structural OH contents in garnet and rutile measured by the stepwise-heating TC/EA-MS method are consistent with those obtained by FTIR. In contrast, the concentrations of structural OH in omphacite, kyanite and quartz measured by the stepwise-heating TC/EA-MS method are higher than those obtained by FTIR. Both equilibrium and disequilibrium H isotope fractionations between garnet and omphacite occur in the eclogite at Bixiling, indicating that the contrasting fractionation behaviors of H isotopes in the two series of minerals are due to differential exchange of H isotopes with internally buffered retrograde fluid during exhumation. This is in concordance with the result from the mineral O isotope study of eclogite [20].

Garnet-omphacite H isotope fractionations are positively correlated with the δD values of total water in garnet, but negatively correlated with those in omphacite (Figure 2). This suggests that the H isotope exchange between garnet and omphacite occurs in a relatively closed system, consistent with the result from the mineral O isotope study [20].

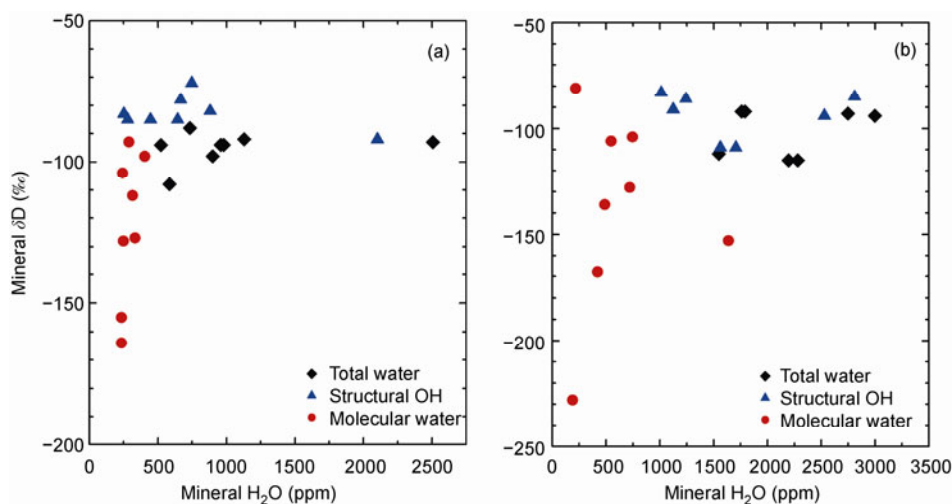


Figure 1 Plot of water content vs. hydrogen isotope composition for different forms of water in garnet and omphacite from eclogites at Bixiling. (a) Garnet; (b) omphacite.

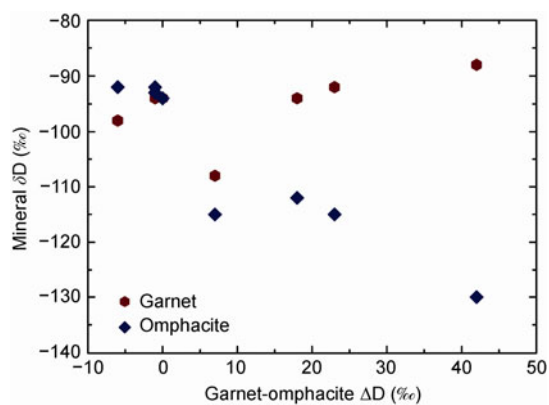


Figure 2 Plot of H isotope fractionations between garnet and omphacite vs. δD values of garnet and omphacite from eclogites at Bixiling.

The structural OH shows similar H isotope fractionations between garnet and omphacite to that of the total water, whereas the molecular H_2O does not seem so. This suggests that the H isotope fractionations between garnet and omphacite are mainly controlled by the structural OH in NAMs, and hence the structural OH is the dominant species in NAMs. The molecular H_2O is depleted in D relative to the structural OH in NAMs from UHP eclogite. This suggests that, during decompression dehydration of the NAMs, the structural OH may transform into the molecular H_2O at first, and then the molecular H_2O was preferentially released from the NAMs. The transformation of structural OH into molecular H_2O is accompanied by kinetic H isotope fractionation during decompression exhumation of the deeply subducted continental crust. In this regard, the mutual transformation of the different forms of water in the NAMs during exhumation of the UHP slice may be one of the major reasons for the variations in the H isotope compositions of NAMs.

3 Core samples of the CCSD project

By taking the advantage of continuous sampling from core samples of the CCSD project and using the TC/EA-MS method, systematic measurements of both H isotope composition and H_2O concentration were carried out for minerals from UHP metamorphic rocks in seven continuous core segments from the CCSD main hole at Maobei in the Sulu orogeny [23]. The results show a large variation in δD values for minerals from UHP metamorphic rocks. Hydrous minerals have δD values of -74‰ to -50‰ for epidote, -120‰ to -54‰ for muscovite, -110‰ to -80‰ for biotite, and -105‰ to -90‰ for amphibole. The NAMs have δD values of -128‰ to -64‰ for garnet, -128‰ to -82‰ for omphacite, -123‰ to -20‰ for rutile, -126‰ to -74‰ for quartz, -123‰ to -108‰ for kyanite, -126‰ to -84‰ for plagioclase, -155‰ to 85‰ for K-feldspar, and -138‰ to -96‰ for magnetite. The variable D-depletion in minerals from the core segments is ascribable to the hydrothermal alteration of their protoliths by meteoric water at elevated temperatures before the continental subduction [20]. Both equilibrium and disequilibrium H isotope fractionations between coexisting minerals occur in the UHP metamorphic rocks, indicating the differential effects of retrograde metamorphism on the H isotope systems of UHP minerals during the exhumation of deeply subducted continental crust. The mineral H isotope compositions of eclogite from the continuous core segments suggest that retrograde fluids were internally buffered in stable isotope composition. This is consistent with the result from the mineral O isotope study of UHP metamorphic rocks [10]. Amphibole and plagioclase in the amphibolite have δD values similar to, or slightly higher than, garnet and omphacite in the adjacent eclogite from the same core segments. This suggests that the retrograde fluid of amphibolite-facies retrogression is

enriched in D relative to the precursor minerals.

Considerable amounts of water occur as both structural OH and molecular H₂O in the NAMs from the CCSD main hole. The water contents of minerals from eclogite and amphibolite are 522–2465 ppm for garnet, 1170–2868 ppm for omphacite, and 1099–3283 ppm for rutile. The water contents of minerals from gneiss are 315–1001 ppm for quartz, 941–1598 ppm for plagioclase, and 890–1781 ppm for K-feldspar. There are obviously negative correlations between water concentrations and δD values for garnet, omphacite and rutile (Figure 3), indicating a preferential loss of D-poor molecular H₂O from the NAMs relative to the structural OH during the decompression exhumation. The retrograde fluid released from the NAMs is depleted in D relative to the precursor minerals. The minerals in the amphibolite have higher δD values, suggesting that the retrograde fluid of amphibolite-facies retrogression is enriched in D and thus derived from the decomposition of D-rich hydrous minerals. Therefore, both the decomposition of hydrous minerals and the exsolution of molecular H₂O and structural OH from the NAMs are responsible for the origin of retrograde fluid during exhumation of the deeply subducted continental crust.

The systematic measurements of water contents for various minerals from the both eclogite and gneiss reveal that the gneiss contains more water than the eclogite [23]. Quantitative calculations of total water contents for gneiss and eclogite were also carried out by using the average water contents calculated statistically by measured water contents for various minerals, revealing that the gneiss generally has higher water content than the eclogite in the presence of hydrous minerals (Figure 4). The gneiss may have higher water contents than the eclogite under the same UHP metamorphic conditions. Thus, the UHP gneiss can release more water than the eclogite during exhumation of the

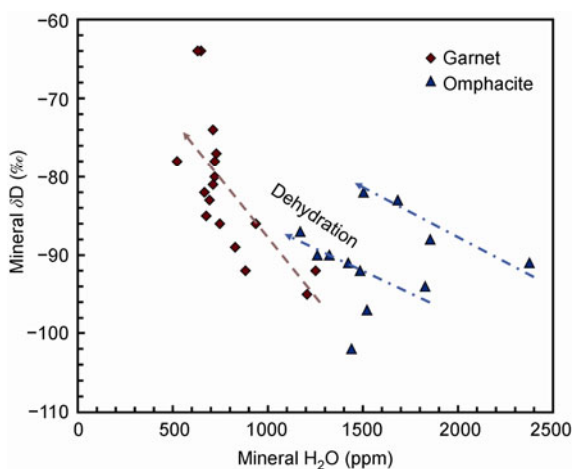


Figure 3 The relationship between total water concentration and hydrogen isotope composition of garnet and omphacite from UHP eclogite in the CCSD main hole [3].

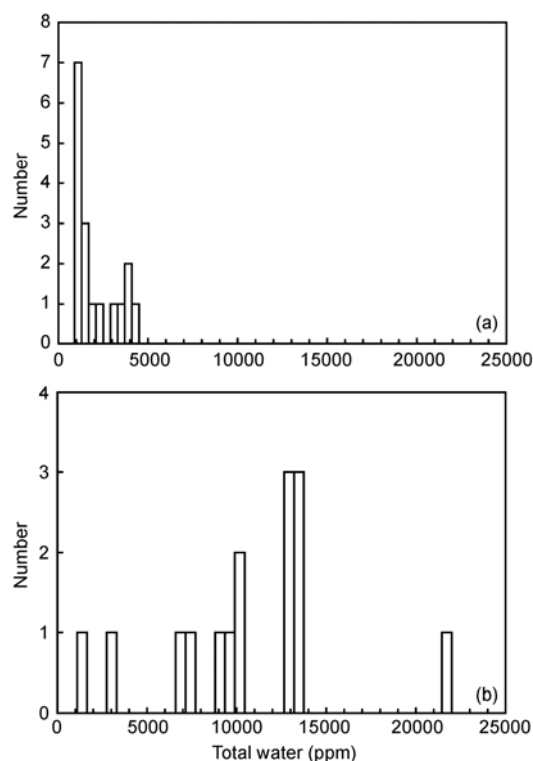


Figure 4 Estimates of total water contents of eclogite and gneiss from the CCSD core segments. (a) Mafic eclogite; (b) felsic gneiss.

deeply subducted continental crust. By decompression dehydration at the contact between eclogite and gneiss, the released water could flow from the gneiss to the eclogite and result in significant hydration of the eclogite adjacent to the gneiss.

4 Mineral water contents of UHP metamorphic rocks

The storage capacity of water in UHP minerals has two important implications for chemical geodynamics. First, the UHP slab can provide a large reservoir of water, which consist of water that was isotopically exchanged on the Earth's surface before subduction [1,3,20]. Second, trace amounts of water in the minerals have disproportional effects on many key chemical and physical properties of UHP minerals and rocks, such as melting temperature, ionic diffusion, element mobility, rheology, electrical conductivity and seismic velocity [2].

By using the TC/EA-MS online technique, we have analyzed the total water contents of minerals in eclogites from the CCSD core samples and five typical outcrops at Bixiling, Qinglongshan, Taohang, Yangkou and Rongcheng in the Dabie-Sulu orogenic belt. The results show variable contents of total water in NAMs: (1) Bixiling contains 252–2102 ppm H₂O in garnet, 1013–2808 ppm H₂O in omphacite, and 540–833 ppm in rutile; (2) Qinglongshan contains

437–1481 ppm H₂O in garnet, 572–2277 ppm H₂O in omphacite, and 944–1774 ppm in rutile; (3) Taohang contains 531–819 ppm H₂O in garnet, 1278–1845 ppm H₂O in omphacite, and 1620–1764 ppm in rutile; (4) Yangkou contains 1395–2392 ppm H₂O in garnet, 2199–3469 ppm H₂O in omphacite, and 804–1371 ppm in rutile; (5) Rongcheng contains 558–1863 ppm H₂O in garnet; and (6) CCSD contains 522–2465 ppm H₂O in garnet, 1170–2868 ppm H₂O in omphacite, and 1099–3283 ppm in rutile.

By using the FTIR method, previous studies determined the concentrations of structural OH in garnet, omphacite and rutile in eclogites from the Dabie-Sulu orogenic belt [10,13,14,17–19]. By using the TC/EA-MS method, the measurement of total water contents was performed for garnet, omphacite and rutile in eclogites from the Dabie-Sulu orogenic belt [10,11,23,24]. The results did not show significant differences between the concentrations of structural OH and total water in the NAMs [3]. However, inspection of these data indicates that these previous analyses of water contents generally were not focused on the same samples. Therefore, by using the both FTIR and TC/EA-MS methods, we have analyzed the water contents of NAMs in eclogites from the both CCSD main hole and five typical outcrops in the Dabie-Sulu orogenic belt. The results show that the TC/EA-MS bulk extraction analyses yield systematically higher water contents than the FTIR analyses for the same samples (Figure 5). This difference suggests that there are significant amounts of water in the form of molecular water in addition to the structural hydroxyl in the Dabie-Sulu UHP minerals. The molecular water occurs either as micro- to nano-scale fluid inclusions, or in the crystal lattice and crystal fracture. During the subduction, one part of the structural hydroxyl and molecular water would occur as modal and cryptic components to be dissolved into the NAMs with increasing pressure, and the other part would be

escaped from the slab with expulsion. It is expected to reach the maximum solubility of water in the NAMs under the maximum pressure [1]. During the exhumation, the exsolution of water from UHP minerals would proceed with the decreasing solubility of water.

By using the FTIR method, Katayama et al. [16] measured the structural OH contents of minerals in the UHP eclogite from Kokchetav, and quantitatively estimated the water contents of eclogite from different subduction depths. The results show that the concentrations of water are about 1650 ppm for diamond eclogite, 950–1210 ppm for coesite eclogite and 490–560 ppm for quartz eclogite. Such differences in water contents suggest that the different forms of water dissolved in the NAMs would be exsolved to form the retrograde fluid and thus decrease the water content of NAMs in response to decompression during exhumation of the deeply subducted continental crust. The systematic investigation of both total water contents and H isotope compositions for UHP minerals from the Dabie-Sulu orogenic belt shows that there are also obviously negative correlations between total water contents and δD values for garnet in UHP eclogites in most areas, similar to those shown in Figure 3. Because of the kinetic effect of H isotope fractionation, there is a preferential loss of D-poor molecular water from the NAMs during exhumation of the UHP rocks. Therefore, such a negative correlation indicates that the large variation of water contents for garnet can be ascribed to the decompression dehydration of minerals during the exhumation [3].

Symplectites show higher water contents but lower δD values than omphacites in the eclogite samples from Yangkou, indicating that the retrograde fluid is dominantly D-poor molecular water. Among the all analyzed eclogites in this study, the Yangkou eclogite shows both the highest water content and δD value in the NAMs. This suggests that

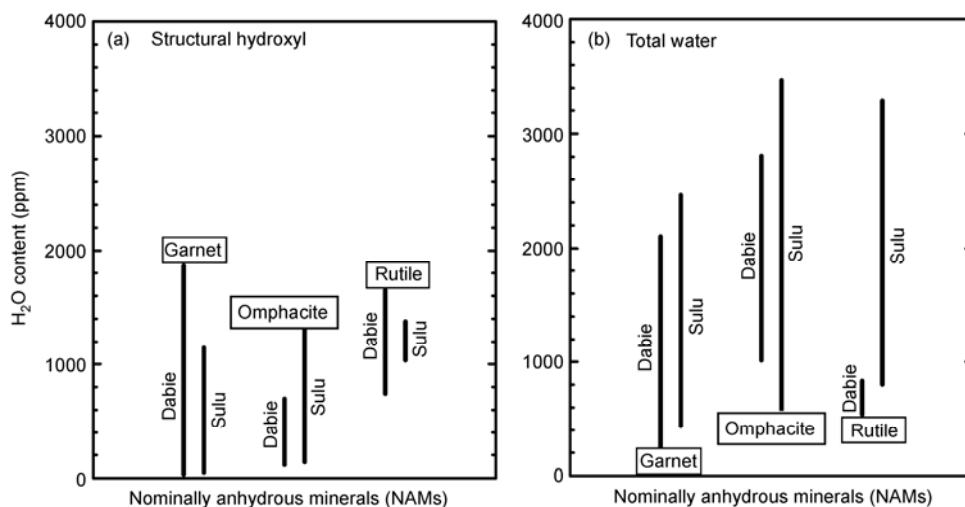


Figure 5 Histograms of concentrations of structural OH and total water in NAMs from eclogites in the Dabie-Sulu orogenic belt. (a) FTIR analysis; (b) TC/EA-MS analysis.

the Yangkou eclogite would have released the least amounts of water from the minerals during exhumation of the UHP slice. In this regard, the highest total water contents of NAMs from the Yangkou eclogite can be taken as the minimum estimates of total water contents in the NAMs under the peak UHP conditions. As such, the measured highest water contents for garnet and omphacite yield the maximum water solubilities of 2500 ppm and 3500 ppm, respectively. Hauri et al. [25] estimated the maximum water contents of 4000–5000 ppm for nominally anhydrous eclogite at 2–4 GPa. The FTIR analyses of natural UHP minerals from both Kokchetav in Kazakhstan and Dabie-Sulu in China gave obviously lower OH contents than the maximum water contents, suggesting that there are significant amounts of water in the form of molecular water besides the structural hydroxyl in minerals from the deeply subducted continental crust.

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