Abstract: Garnet from eclogites often shows very heterogenous and extremely high hydroxyl concentration. Eight eclogite samples were selected from the Sulu ultrahigh-pressure terrane and the Sumdo high-pressure metamorphic belt (Lhasa). The mean hydroxyl concentration in pyrope-rich and almandine-rich garnet varies from 54 to 427 ppm $\text{H}_2\text{O}$ and increases with the retrogression degree of eclogites. TEM observations reveal nanometer-sized anthophyllite exsolutions and clinochlore inclusions in water-rich domains in garnet, where anthophyllite is partly replaced by clinochlore. Because of overlapping of the infrared stretching absorption bands for structural OH in garnet and chlorite, it is impossible to exclude contribution of chlorite inclusions to the estimated hydroxyl concentration in garnet. The broad band near 3400 cm$^{-1}$ is attributed to molecular water and nanometer-sized chlorite inclusions. Anthophyllite exsolutions may be formed by decomposition of hydrous garnet from ultrahigh-pressure eclogites during exhumation. Significant amounts of water can be stored in garnet from massif eclogites in the forms of hydroxyl in garnet and nanometer-sized inclusions of anthophyllite and clinochlore, as well as fluid inclusions. Amphibolite facies retrograde metamorphism can significantly increase both hydroxyl concentration and water heterogeneity in garnet from massif eclogites. The se nano-inclusions in garnet provide a window to trace the water cycle in subduction channels.

Keywords: water; garnet; eclogite; hydroxyl solubility; subduction channel; inclusion; infrared spectrum

1. Introduction

Water can widely exist in nominally anhydrous minerals (NAMs) such as olivine, pyroxene, and garnet, in the form of hydroxyl in lattice defects or molecular water in fluid inclusions (e.g., [1–6]). Subduction zones provide an important pathway to carry water into the earth’s interior and play a critical role in the earth’s water cycle. During subduction of the oceanic lithosphere, water released by breakdown of hydrous minerals will hydrate the mantle wedge and trigger arc volcanism, whereas subduction of the continental lithosphere is characterized by limited fluid activity and lack of coeval arc volcanism [7]. In both cases, several thousand ppm of water can be incorporated in garnet and omphacite, as evidenced by infrared (IR) spectroscopy analysis of eclogites from high-pressure (HP) and ultrahigh-pressure (UHP) metamorphic belts [8–15].

Garnet is one of the most important NAMs in the lower crust and upper mantle. Because water can remarkably decrease viscosity [16,17] but enhance electrical conductivity [18] and Fe-Mg interdiffusion in garnet [19], evaluation of water content in garnet is critical for dynamic modeling and interpretation of electrical conductivity anomalies, as well as for estimation of metamorphic $P-T$ conditions of HP
and UHP rocks. The hydrous components in garnet include both structural OH and non-structural species, which generally can be distinguished from one another by their characteristic stretching frequencies in IR spectra [2,3]. Aqueous fluid inclusions are readily identified by their broad bands near 3400 cm$^{-1}$, which have been excluded in reported water content in garnet. However, invisible inclusions of hydrous minerals in microscopically clear crystal lattice may be very difficult to separate because of the overlapping absorption bands of structural OH in NAMs and hydrous minerals [2].

To avoid confusion, here we use hydroxyl concentration to infer the amount of structural OH, and the total water content for the sum of structural OH, molecular H$_2$O and inclusions of hydrous minerals in garnet.

Hydroxyl concentration in garnet shows wide variations from <1 to >1000 ppm H$_2$O in eclogites from HP and UHP metamorphic belts [6,8–15], and from <1 to several hundred ppm H$_2$O in kimberlite-brought peridotites, eclogites, and megacrysts [20–27]. Extremely high hydroxyl concentration in garnet was observed in UHP eclogites from Kazakhstan (up to 2500 ppm H$_2$O) [8] and the Dabie-Sulu orogen in eastern China (1700–2500 ppm H$_2$O) [10,12,13], implying remarkable water capacity of garnet in subduction zones. Hydroxyl solubility in garnet is a function of pressure, temperature, water fugacity, oxygen fugacity, and chemical composition [28–30]. It is still not clear why hydroxyl concentration in garnet from UHP eclogites in Kazakhstan and the Dabie-Sulu orogen shows great variations and even exceeds the laboratory-derived hydroxyl solubility at high pressure and high temperature.

The IR spectra of eclogitic garnet often exhibit a broad band near 3400 cm$^{-1}$, which has been attributed to the stretching vibration of clusters of molecular H$_2$O in fluid inclusions [5,6,9]. The origin of molecular H$_2$O in eclogitic garnet is still debated. Molecular H$_2$O in garnet from the Dabie-Sulu eclogites is depleted in D relative to the structural OH, and is regarded as intrinsic water because of a preferential loss of the D-poor molecular H$_2$O from garnet during exhumation [6,11,12]. In contrast, for garnet from the Erzgebirge and Fichtelgebirge eclogites in Germany, hydroxyl concentration is <180 ppm in garnet grains free of the broad band at 3400–3450 cm$^{-1}$, and molecular H$_2$O is attributed to secondary eclogite-facies fluid influx postdating the peak metamorphism [14,15]. Using the Gaussian fitting to separate absorption bands in IR spectra of NAMs, previous studies have recognized nanometer-sized inclusions of serpentine and amphibole in olivine [31,32], and clinochlore inclusions in omphacite [33]. Although fine-grained inclusions such as talc, mica, and chlorite are very common in garnet from eclogites (especially near rims and in cracks), these phases are avoided when selecting optically clean areas in garnet for IR analyses. However, transmission electron microscopy (TEM) observations found sodic amphibole exsolutions in garnet from garnet peridotites in the North Qaidam UHP metamorphic belt [34]. To our knowledge, nanometer-sized inclusions of hydrous minerals in garnet have not been systematically studied, and their influence on water content in garnet is still unknown.

This study aims to address the following questions: (1) Why does garnet from HP and UHP eclogites often show heterogeneous and extremely high hydroxyl concentration? (2) Can we find microstructural evidence to distinguish intrinsic and secondary molecular water in garnet? (3) What is the role of garnet in water cycle in subduction channels? We selected garnet from HP and UHP eclogite samples with different compositions and retrogression degrees, and then combined the Fourier transform infrared spectroscopy (FTIR) analysis with TEM observations to investigate heterogeneous water distribution in garnet from eclogites. Nanometer-sized anthophyllite exsolutions and clinochlore inclusions were found in garnet domains with high hydroxyl concentration. Based on hydrogen isotope compositions, metamorphic P-T paths and hydrogen diffusion in garnet, we discussed water capacity in garnet during subduction and exhumation.

2. Sample Description

To examine the influence of retrograde metamorphism and chemical composition on water content in garnet, we selected seven eclogite samples from outcrops and two boreholes of the Chinese Continental Scientific Drilling (CCSD) project at Maobei village in the Sulu UHP terrane, and a highly
retrograded eclogite sample Y from the Sumdo HP metamorphic belt in the Lhasa terrane in Tibet (Table 1). The Sulu eclogites experienced the UHP metamorphism at 220–230 Ma because of continental collision between the Yangtze craton and the North China craton, and exhumed rapidly in a continental subduction channel [35–37]. The Sumdo eclogites show geochemistry of mid-ocean ridge basalts and record HP metamorphism under 2.6–2.7 GPa and 650–730 °C from 239 to 262 Ma, representing remnants of Paleo-Tethyan oceanic crust exhumed from an oceanic subduction channel [38,39]. Although phase equilibrium calculations of Sumdo eclogites yield the peak metamorphic conditions of 2.9 GPa and 610 °C, just above quartz-coesite transition boundary [40], so far UHP index minerals (e.g., coesite, diamond) have not been found in the Sumdo metamorphic belt.

### Table 1. Major-element composition of garnet from the Sulu and Sumdo eclogites.

| Sample | Locality | Grain No. | SiO₂ | TiO₂ | Al₂O₃ | FeO | MnO | MgO | CaO | Cr₂O₃ | NiO | Na₂O | K₂O | Total | Si:12O |
|--------|----------|-----------|------|------|------|-----|-----|-----|-----|------|-----|------|-----|--------|--------|
| X      | Maobei, Sulu | 31       | 40.13 | 0.04 | 24.44 | 10.59 | 0.04 | 14.76 | 10.12 | 0.05 | 0.01 | 0.06 | 0.01 | 100.25 | 2.91 |
| B295   | CCSD-MH, 547.20 m | 10    | 38.14 | 0.24 | 20.64 | 24.59 | 0.18 | 4.85 | 10.96 | - | 0.03 | 0.02 | - | 99.66 | 2.98 |
| MBF1   | Maobei, Sulu | 10 | 41.20 | 0.09 | 22.56 | 9.78 | 0.07 | 13.78 | 12.79 | 0.01 | 0.01 | 0.01 | - | 100.30 | 2.99 |
| MBF3   | Maobei, Sulu | 10 | 41.04 | 0.11 | 22.51 | 9.01 | 0.01 | 13.84 | 13.21 | 0.01 | 0.01 | 0.01 | - | 99.83 | 2.99 |
| B19    | CCSD-PP4, 51.72 m | 10      | 38.14 | 0.14 | 21.01 | 26.03 | 0.26 | 4.46 | 9.39 | 0.01 | 0.01 | 0.04 | - | 99.49 | 3.00 |
| B504   | CCSD-MH, 925.70 m | 9     | 38.29 | 0.16 | 21.24 | 25.59 | 0.28 | 5.25 | 9.10 | 0.01 | 0.01 | 0.03 | - | 99.50 | 2.99 |
| B15    | CCSD-PP4, 45.84 m | 12     | 38.39 | 0.18 | 21.54 | 25.09 | 0.28 | 5.48 | 10.09 | - | 0.02 | 0.02 | - | 100.19 | 2.99 |
| Y      | Sumdo, Tibet | 83 | 38.94 | 0.07 | 22.12 | 19.90 | 0.46 | 7.79 | 10.20 | 0.03 | 0.02 | 0.02 | - | 99.55 | 2.98 |

Note: σ is the standard error of analyzed grains. Si:12O is the number of Si atoms relative to 12 oxygen, which equals to 3 for a normal garnet.

All the samples are coarse-grained, showing garnet-rich and omphacite-rich layers and inequigranular texture (Figure 1). Samples X and B295 are fresh UHP eclogites with coarse-grained garnet and omphacite. Samples MBF1 and MBF3 are fresh garnetites with 80–90 vol.% garnet, which were collected from a garnet-rich layer in the CCSD drilling site. The volume fractions of constituent minerals for each sample were determined by optical microscope observations of thin sections. Samples B19 and B504 are slightly retrograded eclogites with 55–60 vol.% garnet, ~30 vol.% omphacite, 5 vol.% quartz and 5–10 vol.% symplectite. By contrast, retrograded UHP eclogite sample B15 consists of 40 vol.% garnet, 25 vol.% omphacite, 15 vol.% symplectite, 10 vol.% quartz, 3 vol.% phengite, 3 vol.% rutile, 2 vol. % biotite, and 2 vol.% magnetite. Samples B19, B504 and B15 have been strongly deformed with the stretching lineation defined by elongated garnet and omphacite. Retrograded HP eclogite sample Y contains 50 vol.% garnet, 30 vol.% amphibole, 10 vol.% quartz, 5 vol.% phengite, and 5 vol.% rutile (Figure 1).

Compositions of garnet were analyzed using electron microprobe JEOL JXA-8800M at Nanjing University and EPMA-1720H at Zhejiang University, Hangzhou, China. For each sample, at least nine grains were analyzed to obtain the average composition of garnet (Table 1). The composition of garnet varies slightly from grain to grain in a thin section scale, but individual garnet grains are homogenous and free of visible zoning (Figure 2). Three groups of garnet can be distinguished. For eclogite samples in the Sulu UHP terrane, garnet from samples X, MBF1 and MBF3 is pyrope-rich with composition of Prp₅₀₋₅₅ Grs₂₇₋₃₁ Alm₁₅₋₁₈ Adr₀₋₄ Sp₀₋₁, whereas garnet from CCSD samples B15, B19, B295, and B504 is almandine-rich with composition of Alm₅₀₋₅₅ Grs₂₄₋₂₇ Prp₁₈₋₂₁ Adr₀₋₄ Sp₀₋₁. Garnet from retrograded eclogite sample Y in the Sumdo metamorphic belt shows moderate Fe and Mg contents with composition of Al₃₄ Pr₃₀₋₃₅ Grs₂₇₋₃₁ Adr₁₋₄ Sp₀₋₁. Mineral abbreviations in this paper follow Whitney and Evans [41].
Figure 1. (a,b) Specimen and (c–j) thin sections of typical eclogite samples observed using plane-polarized light. Mineral abbreviations: Grt, garnet; Omp, omphacite; Amp, amphibole; Qz, quartz; Ph, phengite; Rt, rutile; Sym, symplectite.
where $A$ is absorbance in cm$^{-1}$, $c$ is integral specific absorption coefficient and equals to 1.39/ppm/cm$^2$ for pyrope-rich garnet, $\varepsilon$ is hydroxyl concentration in mol/L, and $h$ refers to the thickness of a grain [42]. Uncertainties in accuracy of structurally bound OH depend on: (1) absorption coefficient; (2) grain thickness; (3) baseline correction; (4) deduction of the broad band near 3400 cm$^{-1}$. The difference in absorption coefficients between pyrope [42] and grossular [44] is within 10%, suggesting a small compositional effect on the absorption coefficient for our garnet samples. With careful polishing and thickness measurement, the error in grain thickness is within 5%. The baseline correction is realized by using spline and polyline functions embedded in Fityk 0.9.8 with error $<10\%$ [43]. The sum of the integral areas of OH-absorption bands were used to calculate hydroxyl concentration in garnet. On these bases, the overall uncertainty in hydroxyl concentration in garnet is estimated to be less than 30% [10].
we distinguished 11 characteristic narrow bands and labeled them from A to K: (A) 3565–3569 cm\(^{-1}\) with an acquisition time of 0.2–1 s to prevent irradiation damage. (G) 3644–3648 cm\(^{-1}\) in some grains were caused by varying water vapor during experiments [10], which were deleted in spectra of garnet: (I) 3627–3686 cm\(^{-1}\) and a dispersion of 0.1 eV used to calculate di and dark-field images, as well as high-resolution lattice fringe images, were routinely acquired as and an energy-dispersive X-ray (EDX) analyzer with an ultrathin detector window. TEM bright-field United States) was operated at 200 keV with a Schottky emitter as the electron source, which was thickness is less than 100–150 nm. A TECNAI F20 X-Twin TEM (FEI Company, Hillsboro, OR, China) was operated at 200 keV with a Schottky emitter as the electron source, which was equipped with a Gatan imaging filter, a Fishion high-angle annular dark-field detector (HAADF), and an energy-dispersive X-ray (EDX) analyzer with an ultrathin detector window. TEM bright-field and dark-field images, as well as high-resolution lattice fringe images, were routinely acquired as energy-filtered images applying a 20 eV window to the zero-loss peak. High-resolution images were used to calculate diffraction patterns by fast Fourier transform (FFT). EDX analyses were carried out in the STEM thus avoiding mass loss during data acquisition. Linear scans and elemental mapping were acquired using the corresponding X-ray intensities. Electron energy-loss spectroscopy (EELS) was performed with a Gatan GIF imaging filter in the diffraction mode, using a camera length of 700 mm, and a dispersion of 0.1 eV/channel. Spectra were obtained by cumulative acquisition (10–15 spectra) with an acquisition time of 0.2–1 s to prevent irradiation damage.

4. Results

4.1. FTIR Analysis

Given the lack of an integral absorption coefficient for molecular H\(_2\)O and the difficulty in determining the thickness of fluid inclusions, the exact amount of molecular H\(_2\)O in NAMs cannot be obtained from IR spectra. If using the broad band at 3400–3450 cm\(^{-1}\) and the same absorption coefficient as for hydroxyl in garnet (i.e., 1.39/ppm/cm\(^2\)), the amount of molecular H\(_2\)O in garnet was probably overestimated by a factor \(\geq 2\) [15]. To avoid confusion, we used the integral absorbance of the broad band at 3410–3486 cm\(^{-1}\) to compare the intensity of molecular H\(_2\)O in garnet.

Electron-transparent foils for TEM observations were prepared by focused ion beam (FIB) technique [45], utilizing a single-beam device (FEI FIB200 TEM) and a state-of-the-art dual beam system (FEI Helios) operated at German Research Center for Geosciences, Potsdam, Germany. The foil thickness is less than 100–150 nm. A TECNAI F20 X-Twin TEM (FEI Company, Hillsboro, OR, United States) was operated at 200 keV with a Schottky emitter as the electron source, which was equipped with a Gatan imaging filter, a Fishion high-angle annular dark-field detector (HAADF), and an energy-dispersive X-ray (EDX) analyzer with an ultrathin detector window. TEM bright-field and dark-field images, as well as high-resolution lattice fringe images, were routinely acquired as energy-filtered images applying a 20 eV window to the zero-loss peak. High-resolution images were used to calculate diffraction patterns by fast Fourier transform (FFT). EDX analyses were carried out in the STEM thus avoiding mass loss during data acquisition. Linear scans and elemental mapping were acquired using the corresponding X-ray intensities. Electron energy-loss spectroscopy (EELS) was performed with a Gatan GIF imaging filter in the diffraction mode, using a camera length of 700 mm, and a dispersion of 0.1 eV/channel. Spectra were obtained by cumulative acquisition (10–15 spectra) with an acquisition time of 0.2–1 s to prevent irradiation damage.

Figure 3. (a) IR spectra of garnet grain Y-4.1 from sample Y before and after baseline correction, and (b) Gaussian fit for the spectrum after baseline correction.
recognized as the vibration of clusters of molecular water in micro-inclusions (<1–2 µm) [5,6,9–15]. Hence the hydroxyl concentration in garnet is calculated from Equation (1) and the sum of integrated areas of the group I and II bands. As shown in Table 2, the mean hydroxyl concentration in garnet increases with the retrogression degree: from 54–113 ppm H$_2$O in fresh eclogites (samples X, B295, MBF1, and MBF3), 124–127 ppm H$_2$O in slightly retrograded eclogites (samples B19 and B504), to 366–427 H$_2$O ppm in retrograded eclogites (samples B15 and Y). In each thin section, hydroxyl concentration in garnet differs from grain to grain, and does not change systemically from the core to rim (Figure S1). The maximum hydroxyl concentration in garnet grains from retrograded UHP eclogite sample B15 and retrograded HP eclogite sample Y reaches 635 and 1626 ppm H$_2$O, respectively. The standard deviation of hydroxyl concentration in garnet from these samples also increases with the retrogression degree of eclogites, suggesting that retrograde metamorphism can significantly enhance both water content and water heterogeneity in garnet.

Table 2. Water content in garnet from the Sulu and Sumdo eclogites.

| Sample | Lithology                  | Hydroxyl Concentration (ppm H$_2$O) | Primary Structural Water (ppm H$_2$O) |
|--------|----------------------------|-------------------------------------|--------------------------------------|
|        |                            | N  | Min. | Max. | Mean               | N  | Min. | Max. | Mean               |
| X      | UHP eclogite               | 47 | 0    | 356  | 113 ± 89           | 12 | 0    | 84  | 24 ± 22           |
| B295   | UHP eclogite               | 14 | 44   | 124  | 87 ± 22            | 14 | 44   | 124 | 87 ± 22           |
| MBF1   | UHP garnetite              | 11 | 33   | 168  | 66 ± 43            | 7  | 33   | 52  | 41 ± 8            |
| MBF3   | Slightly retrograded UHP eclogite | 25 | 6    | 110  | 54 ± 27 | 17 | 13   | 89  | 46 ± 18 |
| B19    | Slightly retrograded UHP eclogite | 26 | 32   | 511  | 127 ± 106          | 16 | 32   | 139 | 68 ± 30 |
| B504   | Slightly retrograded UHP eclogite | 18 | 36   | 315  | 124 ± 80           | 9  | 36   | 97  | 63 ± 18 |
| B15    | Retrograded UHP eclogite   | 23 | 183  | 635  | 366 ± 139          | 2  | 251  | 254 | 253 ± 3  |
| Y      | Retrograded HP eclogite    | 184| 48   | 1626 | 427 ± 372          | 37 | 55   | 299 | 133 ± 59 |

1 Primary structural water is estimated for garnet grains without the broad 3410–3486 cm$^{-1}$ band. $N$ refers to the number of analyzed grains. The standard deviations of hydroxyl concentration and primary structural water content come from the analyzed grains.

Following Schmädicke and Gose [14], the amount of primary structural water in each sample is estimated from garnet grains without the group III band. The mean value of the amount of primary structural water varies from 24 to 87 ppm H$_2$O in fresh and slightly retrograded eclogites, much lower than 133–253 ppm H$_2$O in retrograded eclogite samples B15 and Y (Table 2). In addition, although hydroxyl concentration in garnet has larger variations than primary structural water, both yield a mode of 75 ppm H$_2$O (Figure 4). Except garnet from fresh UHP eclogite sample B295 that does not exhibit the group III band, both the mean value and the standard variation of primary structural water in garnet are smaller than those of hydroxyl concentration, implying a relationship between the group III band and hydroxyl bands in garnet. Similar with previous studies on eclogitic garnet from the Dabie Mountains [12], the sum of integral absorbance of the group I and group II bands increases with the integral absorbance of the group III band (Figure 5a).

In IR spectra of garnet from massif eclogites [10,12,14,15] and kimberlite xenoliths in southern Africa [20], the group II band near 3570 cm$^{-1}$ is prominent and accompanied with a less intense group I band near 3650 cm$^{-1}$. However, in this study, such trend only occurs for garnet from sample Y and most garnet grains from sample X. The group I band is stronger than the group II band in garnet from samples MBF1, MBF3, B19, B504, and B15 (Figure 5b). Statistically, the absorbance of the group II band and the group III band shows a positive correlation for all samples, especially for garnet from retrograded HP eclogite sample Y (Figure 5c). However, the positive correlation between the group I and group III bands is evident only for samples MBF1, MBF3, B19, B504, and B15 (Figure 5d).

It is worthy to note that among fresh UHP eclogite samples from the Sulu terrane, sample X is characterized by largest hydroxyl concentration of 113 ± 89 ppm H$_2$O, the smallest amount of primary structural water of 24 ± 22 ppm H$_2$O, and weak correlation between the intensity of hydroxyl absorption bands (group I and group II bands) and the group III band (Table 2 and Figure 5). The reason will be investigated using TEM observations.
Figure 4. Histograms show the concentration range and frequency of (a) hydroxyl and (b) primary structural water in garnet from the Sulu and Sumdo eclogites. N is the grain number.

Figure 5. Comparison of the integral absorbance of broad bands in garnet from the Sulu and Sumdo eclogites. (a) The sum of integral absorbance of the group I band at 3627–3686 cm\(^{-1}\) and the group II band at 3565–3603 cm\(^{-1}\) vs. the integral absorbance of the group III band at 3410–3486 cm\(^{-1}\); (b) the group II vs. the group I band; (c) the group II band vs. the group III band; and (d) the group I band vs. the group III band.

4.2. TEM Observations

To examine the origin of the group III band, we cut several foils from optically clean domains in garnet grains from fresh UHP eclogite sample X and retrograded HP eclogite sample Y. Five foils from water-poor domains are associated with or without the group III band, while four foils from water-rich domains always show the group III band. TEM observations reveal that the former is well crystallized and without defects or small inclusions. In contrast, the later often contains some inclusions.

In the TEM foil from eclogite sample X, EDX spectra indicate that anthophyllite and clinochlore appear as nanometer-sized inclusions in garnet, and thin anthophyllite lamellae (100–200 nm thick) occur between clinochlore and garnet (Figure 6). The mineral phases were identified by the indexed diffraction pattern (FFT) from lattice fringe images. Because enstatite and anthophyllite share similar a
and c lattice parameters in the unit-cell parameters and both minerals are orthorhombic, we checked four diffraction patterns from different areas in the same grain. Energy-filtered TEM bright-field images show obvious amphibole characteristics (Figure 7a,b), and the observed average parameters are relatively more compatible with anthophyllite (Table 3). The major-element composition (MgO = 31.62 wt.%, Al₂O₃ = 9.66 wt.%, SiO₂ = 57.01 wt.%, FeO = 0.43 wt.%) from the EDX analysis also supports that the phase is anthophyllite due to high Al₂O₃ content.

In fresh eclogite sample X, anthophyllite exsolution lamellae have been partly replaced by clinoclor, as evidenced by the curved grain boundaries between anthophyllite and clinoclor inclusions (Figure 7a). In contrast to the straight grain boundaries between anthophyllite and garnet (Figure 7a,b), the step-like or curved grain boundaries between clinoclor and garnet suggest replacement of garnet by clinoclor (Figures 7c and 8). However, anthophyllite inclusions are absent in garnet from retrograded eclogite sample Y, where only clinoclor inclusion lamellae were observed in garnet (Figure 8). In addition, nanometer-sized pores are observed in clinoclor from sample X (Figure 7d), implying the existence of clusters of molecular water.

The high-resolution lattice fringe images of the inclusions in garnet (Figure 7a) reveal lattice coupling between garnet and anthophyllite exsolution lamella (Figure 7e), and between anthophyllite and clinoclor (Figure 7f). Diffract patterns show that the (110) plane of garnet, the (020) plane of anthophyllite and the (001) plane of clinoclor are parallel to each other (Figure 7g–i). Using EELS spectroscopy, we examined the water distribution in garnet and the relic anthophyllite exsolution lamella in Figure 7a. The OH peak at approximately 528 eV and prior to the onset of the O–K edge at 532 eV is due to the OH content [49,50]. This OH peak was absent in the host garnet (Figure 9a) and only observed in the anthophyllite exsolution lamella (Figure 9b). This demonstrates contrasting water distribution across the boundary: water-poor garnet and hydrous anthophyllite.

Figure 6. (a,b) Transmission electron microscopy (TEM) images of anthophyllite exsolution lamellae replaced by clinoclor in host garnet from fresh ultrahigh-pressure (UHP) eclogite sample X. The red squares 1, 2 and 3 in (b) indicate the energy-dispersive X-ray (EDX) acquire HAADF areas for phase identification: (c) anthophyllite (Ath), (d) clinoclor (Clc) and (e) garnet (Grt), respectively.
**Figure 7.** TEM images for fresh UHP eclogite sample X. Energy-filtered bright-field images of (a, b) garnet with anthophyllite exsolution lamella partly replaced by clinochlore and (c) step-like grain boundary between clinochlore and garnet. (d) High-angle annular dark-field image of nanometer-sized pores within clinochlore. High-resolution lattice fringe images (HREM) with indexed diffraction patterns (fast Fourier transform FFT) for (e) the interface between garnet and anthophyllite, (f) the interface between anthophyllite and clinochlore, (g) garnet, (h) anthophyllite and (i) clinochlore. The numbers in (e–i) are Miller indices (hkl) of lattice planes. Clc, clinochlore; Grt, garnet; Ath, anthophyllite.

**Table 3.** D-spacing $d_{hkl}$ and angles between adjacent planes for anthophyllite and enstatite.

| Observed Average Parameters | Calculated Anthophyllite | Calculated Enstatite |
|-----------------------------|--------------------------|----------------------|
|                            | hkl                       | hkl                  |
| $d_{hkl}$ (Å)               | $d_{hkl}$ (Å)             |                      |
| 9.23                        | 9.01                     | 9.12                 |
| 4.14                        | 4.12                     | 3.97                 |
| 4.76                        | 4.63                     | 4.41                 |

| Angle degree (°)            | Angle degree (°)          |
|----------------------------|--------------------------|
| $\alpha = 63.1$            | 62.8                     |
| $\beta = 26.5$             | 64.2                     |

Note: The observed average parameters are from four different diffraction patterns of the same garnet grain in sample X, $\sigma$ is the standard deviation. hkl, Miller indices of a lattice plane.
In garnet is supported by a positive correlation between hydroxyl concentration and TiO\textsubscript{2} content in garnet from peridotite xenoliths in southern Africa [20] and from massif eclogites in 4.5. However, based on analysis of IR spectra, hydroxyl may have multiple ways to enter the lattice of garnet [54,55]. For instance, Khomenko et al. [56] found titanium substitution in hydrothermally grown pyrope crystals by Al\textsuperscript{3+} + Si\textsuperscript{4+} + 4O\textsuperscript{2−} = Ti\textsuperscript{4+} + □ + [(OH)\textsubscript{3}O]\textsuperscript{3−}. Crystal chemistry revealed that Ti\textsuperscript{4+} can be substituted into tetrahedral and octahedral vacancies of garnet [57]. This Ti-related hydrogen incorporation mechanism in garnet is supported by a positive correlation between hydroxyl concentration and TiO\textsubscript{2} content in garnet from peridottite xenoliths in southern Africa [20] and from massif eclogites in Erzgebirge and
Fichtelgebirge (Germany) [15]. On the other hand, the iron substitution in garnet by $2[\text{Fe}^{3+}, \text{O}] + \text{H}_2 \rightarrow 2[\text{Fe}^{2+}, \text{OH}]$ is still controversial. Mookherjee and Karato [28] found that at pressure of 5–9 GPa and temperature of 1100–1200 °C, pyrope-rich garnet can have substantial hydroxyl solubility up to 1000 ppm H$_2$O. The y proposed a positive correlation between hydroxyl concentration and Mg$^+$ (Mg$^+$ = Mg/(Mg + Fe) × 100) in garnet. However, there is a negative correlation between hydroxyl concentration and Mg$^+$ in garnet megacrysts crystallized in a kimberlite-like magma at ~5 GPa and ~1100–1400 °C [20].

Compared with previous studies [15,20], the correlations between hydroxyl concentration and TiO$_2$ content or Mg$^+$ are absent for our samples (Figure 10a,b). If we only take into account of garnet from fresh and slightly retrograded UHP eclogite samples, the amount of primary structural water correlates with TiO$_2$ content positively (Figure 10a). This result confirms the Ti-related hydrogen substitution mechanism in natural garnet. In addition, our garnet samples from fresh and slightly retrograded UHP eclogites yield a pronounced negative correlation between hydroxyl concentration and CaO content (Figure 10c), which is consistent with study on garnet pyroxenites in the Sulu UHP terrane [58] but in contrary to observations for eclogitic garnet from the Erzgebirge and Fichtelgebirge complexes [15].

**Figure 10.** Mean primary structural water content versus (a) TiO$_2$ content and (b) Mg$^+$ in garnet, and (c) mean hydroxyl concentration versus CaO content in garnet from the Sulu and Sumdo eclogite samples. The dashed line is the least squares fit to the data of fresh UHP eclogites and slightly retrograded eclogites.
To check this discrepancy, we compared our data with previous studies on garnet from different localities [8,10,12,13,15,59] (Figure 11). Hydroxyl concentration in garnet from eclogites and garnet pyroxenites shows remarkable variations, especially for samples from the Dabie-Sulu orogen (Figure 11a). However, the correlation between hydroxyl concentration and CaO content in garnet is very weak, no matter for all samples (Figure 11a) or for eclogitic garnet with hydroxyl concentration less than 300 ppm H2O (Figure 11b). For garnet pyroxenites, garnet is relatively Ca-rich and shows lower hydroxyl concentration with increasing CaO content. Garnet from retrograded eclogite samples B15 and Y does not follow any above correlations between hydroxyl concentration and major element content, implying that retrograde metamorphism has erased the original influence of mineral chemistry on hydroxyl concentration in garnet.

Liu et al. [13] divided garnet grains from ten UHP eclogites in the Dabie Mountains into two classes according to their hydroxyl concentration. They found that when hydroxyl concentration in garnet is higher than 400 ppm H2O, hydroxyl concentration in garnet shows a positive correlation with the Ca atoms per 12 anions, and a negative correlation with the Si, Mg, and Fe2+ atoms per 12 anions. However, such relationship is absent for garnet with ≤400 ppm H2O. In this study, both Mg-rich and Fe-rich garnet from the Sulu and Sumdo eclogites can contain high hydroxyl concentration. Unfortunately, the proposed correlation between chemical composition and hydroxyl concentration in water-rich garnet is not observed in our samples (Figure S2).

![Figure 11. Mean hydroxyl concentration versus CaO content for garnet from (a) eclogites and garnet pyroxenites, and (b) eclogite samples with mean hydroxyl concentration <500 ppm H2O. Garnet samples are from massif eclogites in the Dabie-Sulu orogen [10,11,13,59], the Kokchetav massif [8] and the Erzgebirge and Fichtelgebirge (EG + FG) complexes [15], and from garnet pyroxenites in the Sulu UHP terrane [58].](image)

In addition, Bell and Rossman [20] noticed that the peak position of the strongest band near 3570 cm⁻¹ (the group II band) shifts to lower wavenumber from 3580 to 3565 cm⁻¹ with decreasing Mg# in garnet megacrysts. In our samples, only UHP eclogite sample X and retrograded HP eclogite sample Y show the predominance of the group II band over the group I band (Figure 5b). However, for Mg-rich garnet from sample X, there is no any correlation between the peak position of the group II band and Mg# (Figure 12a,b). This trend is only observed for garnet grains without the group III group from sample Y (Figure 12d). Further experiments are needed to explore the influence of Fe-related hydrogen substitution in garnet.

It is noteworthy that the narrow bands A to K have fixed wavenumbers despite of different hydroxyl concentration in garnet (Figure 3). To investigate the origin of these narrow bands, we define the strength coefficient of a narrow band (η) as the ratio between the integrated area of a narrow band (Δn) and the integrated area of total characteristic bands of hydroxyl (Δh):

\[ \eta = \Delta_n / \Delta_h \] (2)
For garnet from Mg-rich eclogite sample X, the strength coefficients of narrow bands C and K decrease with Fe$^{2+}$ concentration (Figure 13a,b), whereas that of the narrow band I decreases with Cr concentration (Figure 13c). However, such relationships are ambiguous in garnet from retrograded eclogite sample Y, implying different substitution mechanisms due to the compositional change. For other narrow bands, we did not find any correlation between the strength coefficients and garnet compositions, probably because of the limited data. The infrared absorption peak of anthophyllite is near 3675 cm$^{-1}$ [60] (Figure 14a), which agrees with the narrow peak J at 3670–3678 cm$^{-1}$. Given the stability of wavenumbers of the narrow bands with varying hydroxyl concentration, these narrow bands could be used as “fingerprint peaks” to trace the influence of different cations on hydroxyl substitution in garnet.

**Figure 12.** The peak position of the group II band vs. Mg# in garnet from UHP eclogite sample X and retrograded HP eclogite sample Y. (a,c) for all grains, (b,d) for grains without the group III band.

**Figure 13.** Cont.
Figure 7d, which can provide the space for clusters of molecular water. It is worthy to note that Figure 7. Anthophyllite exsolution lamellae locally appear in garnet from UHP eclogite sample X and than in FTIR analysis. TEM than in FTIR analysis. group III band and hydroxyl enrichment by hydrogen di clinochlore inclusions are absent in some foils from water-rich domains, where the group III band still occurs. However, in water-rich domains in garnet, we found nanometer-sized pores in clinochlore inclusions and a band at 3565–3610 cm

Figure 13. Relationships between the strength coefficient of narrow bands and major element compositions for fresh eclogite sample X. (a) The strength coefficient of narrow band C vs. Fe$^{3+}$ atoms per 12 anions, (b) the strength coefficient of narrow band K vs. Fe$^{2+}$ atoms per 12 anions, and (c) the strength coefficient of narrow band I vs. Cr atoms per 12 anions.

5.2. Origin of the Broad Band Near 3400 cm$^{-1}$

A broad band near 3400 cm$^{-1}$ (group III band) in IR spectra of synthetic pyrope [61] and garnet crystals from diamondiferous UHP rocks [9] has been attributed to the vibration of (H$_2$O)$_n$ clusters in fluid inclusions for a long time. Associated with the broad IR band near 3440 cm$^{-1}$, clusters of water molecules were found as heterogeneously distributed inclusions in eclogitic garnet with the size to 0.063 µm in bright-field TEM images [5]. Since then, the widespread group III band in IR spectra of eclogitic garnet was interpreted as molecular water in fluid inclusions [9–15]. As shown in Figure 5, although the broad group III band was excluded in calculation of hydroxyl concentration, it has strong influence on hydroxyl absorption bands in garnet. Hence its origin, either intrinsic or secondary, is critical for tracing fluid activity of UHP rocks in subduction channels.

In this study, water-poor domains in garnet are well crystallized, free of inclusions, and with or without the group III band. In contrast, water-rich domains in garnet always show the group III band, and often contain nanometer-sized anthophyllite exsolution lamellae and clinochlore inclusions (Figure 7). Anthophyllite exsolution lamellae locally appear in garnet from UHP eclogite sample X and have been partly replaced by clinochlore, whereas clinochlore lamellae widely occurs in garnet from both UHP eclogite sample X and retrograded HP eclogite sample Y. The OH stretching absorption bands of clinochlore and chlorite include a broad band at 3407–3453 cm$^{-1}$ with the FWHM >160 cm$^{-1}$, and a band at 3565–3610 cm$^{-1}$ with the FWHM <100 cm$^{-1}$ [33,62–64] (Figure 14a). This means when garnet contains nanometer-sized inclusions of chlorite minerals, the overlapping absorption bands of garnet and chlorite will make them indistinguishable in IR spectra (Figure 14b). The refore, even using the Gaussian fit to exclude the group III band, the remaining contribution of chlorite minerals to the group II band at 3565–3603 cm$^{-1}$ cannot be ruled out. This explains why the absorbance of the group III band shows a positive correlation with the sum of absorbance of group I and II bands (Figure 5a) and with the absorbance of group band II for garnet (Figure 5c), as observed for eclogitic garnets from the Dabie Mountains [12] and the Erzgebirge and Fichtelgebirge complexes [14,15].

We did not directly observe the clusters of molecular water in TEM observations as Su et al. [5]. However, in water-rich domains in garnet, we found nanometer-sized pores in clinochlore inclusions (Figure 7d), which can provide the space for clusters of molecular water. It is worthy to note that clinochlore inclusions are absent in some foils from water-rich domains, where the group III band still occurs. This can be explained by the sole contribution of molecular water in fluid inclusions to the group III band and hydroxyl enrichment by hydrogen diffusion, or heterogenous distribution of fluid inclusions and/or clinochlore inclusions in garnet because of the much smaller observation area in TEM than in FTIR analysis.
A combination of thermal conversion element analyzer (TC/EA) with isotope ratio mass spectrometry (MS) allows determination of both hydrogen isotopes and the total water content of garnet [65]. During TC/EA-MS analyses on garnet, preheating at 350 °C for 4 h removed the most intensity of the group III band without loss of structural OH, then preheating at 600 °C for 6 h totally removed the group III band but also caused partial loss of structural OH [65]. This suggests that molecular H₂O has a much faster diffusion rate than structural OH in garnet, as observed in water diffusion experiments in silicate glasses [66–68]. Gong et al. [65] attributed the change of the group III band to the loss of molecular H₂O during the stepwise heating process, but did not explain why the final loss of molecular H₂O in garnet occurred until 600 °C and was accompanied with partial loss of structural OH. The breakdown temperature of chlorite minerals is a function of composition, pressure, and oxygen fugacity. For intermediate magnesium-iron chlorites of the clinochlore-daphnite series, the breakdown temperature of chlorites decreases with decreasing pressure and smaller Mg# [69]. Extrapolating experiments of Mconie et al. [69], the upper stability limit of clinochlore is ~600 °C at room pressure and Ni-NiO buffer. The refore, the two-step loss of the group III band in the TC/EA-MS analyses of garnet [6,11,12,65] can be better explained by the loss of molecular H₂O in micro-inclusions at 350 °C, and the dehydration reaction of clinochlore inclusions at 600 °C.

Gong et al. (2007) [65] found δD values of ~86‰ for structural OH and ~101‰ for molecular H₂O in a garnet crystal from the Dabie UHP eclogite. The negative correlations between the total water content and δD values for garnet, omphacite, and rutile in eclogites from the CCSD borehole demonstrate a preferential loss of the D-poor molecular water from the NAMs by diffusion relative to the structural OH during exhumation [11,70]. Meanwhile, amphibole and plagioclase in amphibolites have δD values similar to, or greater than garnet and omphacite from the adjacent eclogites, and epidote and muscovite have higher δD values than amphibole. The refore, there are two origins of
retrograde fluid with contrasting hydrogen isotope compositions: D-depleted fluid by exsolution of molecular H$_2$O and structural OH from NAMs, and D-rich fluid by decomposition of hydrous minerals from surrounding rocks during amphibolite-facies retrogression metamorphism. Statistically, the δD values of molecular H$_2$O in eclogitic garnet show larger variations than the structural OH, suggesting dual origins of molecular H$_2$O in garnet [70].

As shown in Table 2 and Figures 5 and 10, garnet from fresh and slightly retrograded eclogites is characterized by relatively low hydroxyl concentration, weak correlation between the intensity of the group-III band and the group II band, and evident correlations of the amount of primary structural water with TiO$_2$ content. In contrast, garnet from retrograded eclogites shows very high hydroxyl concentration, positive correlation between the intensity of the group-III band and the group II band, and independence of the amount of primary structural water on mineral chemistry. Hence we propose that water related with the group III band in garnet predominantly came from the intrinsic D-depleted fluid in NAMs for fresh and slightly retrograded eclogites, but includes both intrinsic D-depleted fluid in NAMs and secondary D-rich fluid from hydrous minerals for retrograded eclogites.

Micrometer-sized aqueous fluids with variable salinities and gas species (N$_2$-, CO$_2$-, or CH$_4$-rich) have been found as primary inclusions in garnet from the Dabie-Sulu eclogites [71,72]. The great diversity of fluid compositions and large-scale $^{18}$O depletion in UHP rocks from the Dabie-Sulu orogen indicate very limited fluid-rock interaction during peak metamorphism and retrograde metamorphism [73]. For UHP eclogites and surrounding gneisses in the Sulu terrane, the δD values for the coexisting hydrous minerals [70] do not follow the D-enrichment sequence derived from experimental studies for equilibrium H isotope fractionation at $T > 500$ °C [74–76], which can be attributed to the disequilibrium H fractionation in coexisting minerals because of the different rates of H diffusion. Similar with the oxygen isotope observations, the H isotope exchange between garnet and omphacite also occurred in a relatively closed system during exhumation of eclogites [70].

5.3. Origin of Nanometer-Sized Inclusions in Garnet

A striking observation from our experiments is anthophyllite inclusions interlayered between clinochlore and garnet in foils cut from fresh UHP eclogite sample X (Figures 6 and 7). The well-preserved microstructure of anthophyllite within garnet implies its exsolution origin. Sodic amphibole exsolution lamellae in garnet have been documented in garnet peridotites from the North Qaidam UHP metamorphic belt, and was interpreted as decomposition of sodic and OH-bearing parental majoritic garnet to amphibole, rutile and “normal” garnet during exhumation from a depth large than 200 km ($P > 7$ GPa) [34,77]. Sakamaki et al. [78] found similar sodic amphibole exsolution lamellae in water-poor pyrope from kimberlites in the Colorado Plateau. The y proposed that breakdown of hydrous Na-rich majoritic garnet will produce amphibole lamellae and dehydrate garnet during exhumation to depths shallower than 100 km by the following reaction:

$$(\text{Mg, Ca, Na})_3(\text{Al}_{2-x}, \text{Mg}_x)_2\text{Si}_3\text{O}_{12-2x}(\text{OH})_{2x} \rightarrow x\text{NaCa}_2(\text{Mg}_4\text{Al})\text{Si}_6\text{Al}_2\text{O}_{22}(\text{OH})_2 + (1-2x)(\text{Mg, Ca})_2\text{Si}_3\text{O}_{12}$$ (3)

In contrast to the sodic amphibole exsolution lamellae in the size of tens to hundreds microns within “original” majoritic garnet [34,77,78], anthophyllite exsolution lamellae in garnet from sample X are nanometer-sized and invisible in an optical microscope. Hence it is impossible to calculate the majoritic component of garnet. Eclogites from the CCSD boreholes and the Maobei village in the Sulu terrane experienced UHP metamorphism at 770–840 °C and 3.2–4.0 GPa (>100 km) [79]. Garnet in sample X shows relatively small Si content (2.91 for 12 oxygen) (Table 1) and low water content next to the hydrous anthophyllite exsolution (Figure 9). The refore, anthophyllite exsolution may be caused by decomposition of hydrous garnet during exhumation:

$$\text{hydrous garnet} \rightarrow \text{anthophyllite} + \text{“normal” water-poor garnet.}$$ (4)
Substitution of H⁺ to Si⁴⁺ in the form of (OH)₄⁺ cluster could meet the Si saturation in garnet [52,53]. During exhumation process, further fluid activity will result in alteration of anthophyllite to clinohlore by addition of water and Al content from the host garnet or surrounding hydrous minerals:

\[ \text{anthophyllite} + \text{H}_2\text{O} + \text{Al}^{3+} \rightarrow \text{clinohlore} \]  \( \text{(5)} \)

Different from fluid inclusions that may enhance hydroxyl concentration in nearby domains in garnet by hydrogen diffusion [15], the occurrence of nanometer-sized anthophyllite exsolution lamellae is accompanied by dehydration of nearby domains in garnet (Figure 9), although the IR spectrum yields high hydroxyl concentration in the 40 × 40 μm² analyzed area. Our TEM images also record the partly replacement of anthophyllite by clinohlore in garnet from UHP eclogite sample X (Figure 7a,b). The refore, these nanometer-sized anthophyllite exsolution lamellae and clinohlore inclusions in garnet preserved the evidence of water transportation within the lattice of garnet during exhumation. When fluid influx is sustainable, excess water will be stored as clusters of molecular H₂O in nanometer-sized pores in clinohlore inclusions (Figure 7d). In contrast, garnet from retrograded HP eclogite sample Y is lack of anthophyllite exsolution lamellae but often contains clinohlore inclusions, suggesting that clinohlore is the dominant hydrous mineral within garnet at lower pressure. All these solid and fluid inclusions are responsible for the heterogeneous water distribution in garnet from a grain scale to a thin section scale.

5.4. Contribution of Garnet to the Water Cycle

In order to estimate the contribution of garnet to the deep water cycle, we compared hydroxyl concentration in natural garnet with the calculated hydroxyl solubility in pyrope under different P-T conditions. Lu and Keppler [29] found that hydroxyl solubility (cOH) in pyrope increases with pressure and can be described by the equation up to 10 GPa:

\[ c_{\text{OH}} = A_{\text{OH}}^i \text{H}_2\text{O} \exp \left( \frac{-\Delta E + P\Delta V}{RT} \right) \]  \( \text{(6)} \)

where \( f_{\text{H}_2\text{O}} \) is the water fugacity, \( R \) is the gas constant, \( P \) is pressure, \( T \) is temperature, \( \Delta E \) is the reaction enthalpy, \( A \) is 0.679 ppm/bar⁰.⁵, and \( \Delta V \) is 5.71 cm³/mol at 1000 °C. At 1000 °C and 2 GPa, the enthalpy of the hydroxylation reaction \( \Delta H \) is 14 kJ/mol. Using their experimental data, \( \Delta E \) is estimated as 2580 J/mol and \( A \) is 0.866 ppm/bar⁰.⁵ for different temperatures. The water fugacity \( f_{\text{H}_2\text{O}} \) was determined using the analytical solution [80]:

\[ \ln f_{\text{H}_2\text{O}} = \left[ \ln \rho + A_{\text{res}}^i \frac{RT}{P} \right]_\rho + \ln(\rhoRT) - 1 \]  \( \text{(7)} \)

where \( A_{\text{res}}^i \) is residual Helmholtz energy, \( \rho \) is molar density (n/V). The molar volume of pure water at different pressure and temperature was estimated by the equation of state [81]:

\[ \frac{A_{\text{res}}^{i}}{RT} = c_1 \rho + \frac{1}{c_2} + \frac{1}{c_3} + \frac{1}{c_4} + \frac{1}{c_5} - \left( \frac{c_7}{c_8} \right) \exp(-c_9 \rho) - 1 \]  \( \text{(8)} \)

where \( c_{1-10} \) refer to different temperature-related parameters:

\[ c_i = c_{i1} T^{-4} + c_{i2} T^{-2} + c_{i3} T^{-1} + c_{i4} + c_{i5} T + c_{i6} T^2. \]  \( \text{(9)} \)

The coefficients \( c_{ij} \) in Equation (9) for H₂O were provided by Pitzer and Sterner [81]. We adopted representative geothermal profiles from different tectonic settings: a P-T path of the Sulu UHP belt [35], the Western Superior Province for a cold and stable Archean craton, the Dabie Mountains for a normal crust after Triassic continental collision, and the North Jiangsu basin for an active extensional basin [82].
The average crustal and mantle densities are 2.85 g/cm$^3$ and 3.3 g/cm$^3$, respectively. As shown in Figure 15b, hydroxyl solubility in pyrope increases with depth for all tectonic settings, with the highest value in the North Jiangsu basin because of its highest temperature at depth <120 km. The cold thermal structure of the Western Superior Province is comparable with the P-T path of the Sulu UHP rocks during subduction, resulting in the lowest hydroxyl solubility in pyrope. During exhumation of the Sulu UHP rocks, hydroxyl solubility in pyrope will be slightly higher because of the increased temperature. At a depth of 150 km, the hydroxyl solubility in pyrope can reach 180 ppm beneath the Dabie Mountains and the North Jiangsu basin, but only about 150 ppm beneath the Western Superior Province. However, in experiments of Mookherjee and Karato [28], water solubility in pyrope-rich garnet can reach 1000 ppm at pressure of 5–9 GPa and temperature of 1100–1200 °C, about five times the value from Lu and Keppler [29].

Hydroxyl concentration in natural garnet from eclogites shows larger variations from nearly dry to 2500 ppm H$_2$O ([6,8–10,12–15,59]; this study). To avoid overlapping of data points, we only used the mean hydroxyl concentration of each sample and excluded the samples with hydroxyl concentration >500 ppm H$_2$O in Figure 15b. All garnet samples with extremely high hydroxyl concentration come from retrograded eclogites with different chemical compositions. It is interesting to notice that some slightly retrograded eclogites such as samples B19 and B504 contain hydroxyl concentration close to the calculated water solubility of pyrope. Our study indicates that compared with synthetic garnet in water solubility experiments, garnet from massif eclogites often contain randomly distributed nanometer-sized inclusions of chlorite minerals and fluid inclusions, which can significantly enhance hydroxyl concentration and water heterogeneity in garnet. By contrast, garnet from kimberlite-brought peridotite xenoliths in cratons [23–26] and garnet megacrysts from kimberlite-like magma (15–74 ppm H$_2$O) [27] contain <100 ppm H$_2$O, far below the water solubility of pyrope at depth (Figure 15b).

Lu and Keppler [29] found that at Fe-FeO buffer conditions, water solubility in pyrope is only about 50% to 70% of the values with the Ni-NiO buffer, demonstrating the important influence of oxygen fugacity on water solubility in garnet. For eclogites in UHP terranes, retrograde metamorphism has
elevated $\text{Fe}^{3+}/\Sigma \text{Fe}$ ratios of eclogites because of oxidizing fluids during exhumation [83]. In contrast, peridotite xenoliths from kimberlite pipes were subjected to more reduced conditions at great depths [84], which will result in a smaller water solubility in garnet from the cratonic lithospheric mantle than from subduction zones. In addition, kimberlite magmas rise at a rate of 15–20 km/h [85]. The extremely rapid transportation of peridotite xenoliths and megacrysts by kimberlite magmas will prevent effective hydrogen diffusion and alteration in garnet.

On the other hand, exhumation rates of UHP terranes vary from place to place and often include two stages: an initial fast exhumation from the mantle depth to ~35 km, and a slow exhumation from the lower crust to the upper crust. In average, the exhumation rates of UHP rocks are estimated to be 5–11.3 mm/yr for the Dabie-Sulu orogenic belt [37], ~10 mm for the Western Gneiss Region [86], ~20 mm/yr for the Kachin Valley in the Himalayan orogen [87], and 16–50 mm/y for the Alpe Arami peridotites in the central Alps [88]. Decompressional dehydration of zoisite, phengite and lawsonite can supply enough aqueous fluid for water enrichment in omphacite and garnet during the initial exhumation [73]. The water-rich omphacite and garnet will experience decompressional dehydration and release D-depleted water during exhumation process [70]. Similar to anthophyllite exsolutions and clinochlore inclusions in garnet, nanometer-sized inclusions of clinochlore and amesite in omphacite from eclogites could also be formed during exhumation and result in overestimation of hydroxyl concentration in omphacite [33]. Hence, it is necessary to re-estimate the partition coefficient of hydrogen between garnet and omphacite in mantle conditions.

In addition, although hydroxyl concentration in one garnet grain may change greatly, there is no systematic change from the core to the rim in our garnet samples (Figure S1). Hydrogen diffusion in garnet includes bulk diffusion and grain boundary diffusion [89,90]. Experimental data show that the hydrogen diffusion in garnet follows the Arrhenius relation [91]. The effect of hydrogen diffusion can be quantified by the diffusional length scale:

$$l = \sqrt{D_{\text{eff}}t}$$

where $l$ is the characteristic distance in meter, $D_{\text{eff}}$ is the effective diffusion coefficient of garnet in m$^2$/s, and $t$ is time in second. We applied the linear diffusion model to calculate the diffusional length scale in garnet. When temperature is higher than 700 °C, it takes less than 1 Ma for hydrogen diffusing away from the garnet-rich area in a subduction zone (Figure 16a). When temperature is less than 700 °C, the diffusion distance of hydrogen in garnet becomes very limited in a geological time scale. If using the sphere diffusion model [92], it will take ~2 Ma for the loss of 50% hydrogen in garnet when temperature is less than 600 °C (Figure 16b). It is worthy emphasizing that when the surrounding rocks are also rich in H, the H concentration gradient is rather favorable to a diffusion of H towards the garnet-rich area. This is the case in the late exhumation stage, as shown by incorporation of secondary fluid from hydrous minerals into garnet from retrograded eclogites.

Because the relatively low temperature and the rapid exhumation rate of UHP rocks in subduction channels at mantle depths (i.e., under eclogite facies metamorphism in the early exhumation stage), we propose that the critical temperature for the ignorable hydrogen diffusion in garnet is 600 °C in a geological time scale, corresponding to amphibolite facies retrograde metamorphism (Figure 15a). Hence the measured water content in garnet reflects in situ water concentration in garnet under amphibolite facies retrogression. Given wide stability conditions of garnet, the released water by both hydrous minerals (e.g., zoisite, phengite and lawsonite) and NAMs (omphacite and garnet) during retrograde metamorphism could be preserved in the crystal structure of garnet in different forms (hydroxyl in garnet and hydrous mineral inclusions, and molecular water in fluid inclusions). This will significantly decrease the viscosity of eclogites and facilitate their exhumation in a subduction channel [16,17]. Therefore, garnet is an important candidate to transport water into the mantle transition zone and to carry water back from great depths to the shallow level through the subduction channel.
will be incorporated into clinochlore inclusions by reaction of anthophyllite with water, and then appear as clusters of molecular water and chlorite inclusions, which will result in very high hydroxyl concentration in natural garnet.

Some narrow bands can be used to trace different substitution mechanisms of hydrogen due to the compositional change. TEM observations of water-rich domains in garnet reveal nanometer-sized anthophyllite exsolution lamellae, clinochlore inclusions, and pores within clinochlore inclusions. The broad band near 3400 cm\(^{-1}\) in garnet can be due to clusters of molecular water and chlorite inclusions, which will result in very high hydroxyl concentration in natural garnet.

The co-existence of water-poor garnet and hydrous anthophyllite in garnet with relatively small Si content suggests substitution of Si\(O_4^{4-} \rightarrow (OH)_4^{3-}\) in hydrous garnet at great depths, and formation of anthophyllite exsolutions by decomposition of hydrous garnet during exhumation. The extra water will be incorporated into clinochlore inclusions by reaction of anthophyllite with water, and then appear as clusters of molecular water in fluid inclusions. Heterogenous hydroxyl concentration in garnet (<1 to 2500 ppm H\(_2\)O) from eclogites recorded very limited fluid-rock interaction and the “frozen” water distribution during amphibolite facies retrograde metamorphism in subduction channels.

**6. Conclusions**

We measured the hydroxyl concentration in garnet from eight eclogite samples in the Sulu UHP terrane and the Sumdo HP metamorphic belt in China. Using Gaussian functions, IR spectra of garnet were fitted by three groups of broad bands and superimposed narrow bands. Hydroxyl concentration in garnet increases with the retrogression degree of eclogites from 54 to 427 ppm H\(_2\)O. The amount of primary structural water in garnet shows a positive correlation with TiO\(_2\) content for fresh and slightly retrograded UHP eclogites. Some narrow bands can be used to trace different substitution mechanisms of hydrogen due to the compositional change. TEM observations of water-rich domains in garnet reveal nanometer-sized anthophyllite exsolution lamellae, clinochlore inclusions, and pores within clinochlore inclusions. The broad band near 3400 cm\(^{-1}\) in garnet can be due to clusters of molecular water and chlorite inclusions, which will result in very high hydroxyl concentration in natural garnet.

The co-existence of water-poor garnet and hydrous anthophyllite in garnet with relatively small Si content suggests substitution of Si\(O_4^{4-} \rightarrow (OH)_4^{3-}\) in hydrous garnet at great depths, and formation of anthophyllite exsolutions by decomposition of hydrous garnet during exhumation. The extra water will be incorporated into clinochlore inclusions by reaction of anthophyllite with water, and then appear as clusters of molecular water in fluid inclusions. Heterogenous hydroxyl concentration in garnet (<1 to 2500 ppm H\(_2\)O) from eclogites recorded very limited fluid-rock interaction and the “frozen” water distribution during amphibolite facies retrograde metamorphism in subduction channels.

**Supplementary Materials:** The following are available online at http://www.mdpi.com/2075-163X/10/5/410/s1,
Figure S1: Variations of the position of the group I band and hydroxyl concentration in garnet crystals; Figure S2: Correlation between chemical composition and hydroxyl concentration in garnet from fresh eclogite sample X and retrograded eclogite sample Y.

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