REVISION 2

Water transport by subduction: clues from garnet of Erzgebirge UHP eclogite

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Abstract

A key question concerning the water budget of Earth's mantle is how much water is actually recycled into the mantle by the subduction of eclogitized oceanic crust. Hydrous phases are stable only in quartz eclogite not coesite eclogite so that water transport to greater depths is mainly governed by structural water in omphacite and garnet. Here we explore if garnet can be used as a proxy to assess the amount of this water. Available data on the water contents of garnet in coesite eclogite vary over orders of magnitude, from a few up to ca. 2000 ppm. By implication, the maximum bulk-rock water contents are unrealistically high (wt% level). New data from the Erzgebirge indicate moderate amounts of structural H_2O stored in garnet (43 - 84 ppm), omphacite (400 - 820 ppm), and in the bulk coesite eclogite (ca. 280 - 460 ppm). Higher garnet water contents occur, but these are not primary features. They are related to molecular water in fluid inclusions that can be attributed to eclogite-facies fluid influx postdating the metamorphic peak. Fluid influx also caused the uptake of additional structural water in garnet domains close to fluid inclusions. Such secondary H_2O incorporation is only possible in the case of primary water-deficiency indicating that garnet hosted less water than it was able to store. This is insofar astonishing as comparably high H_2O amounts are liberated by the breakdown of prograde eclogite-facies hydrous minerals as a result of ultra-high pressure (UHP) metamorphism. Judging from Erzgebirge quartz eclogite, dehydration of 5 - 10 % hydrous minerals (± equal portions of zoisite + calcic amphibole) produces 1500 - 3000 ppm water. We infer that the largest part of the liberated water escaped, probably due to kinetic reasons, and hydrated exhuming UHP slices in the hanging-wall. Depending on the physical conditions, water influx in eclogite during exhumation (i) produces fluid inclusions and simultaneously enhances the structural water content of nominally anhydrous minerals – as in the Erzgebirge – and/or (ii) it may give rise to retrograde hydrous minerals. We conclude that eclogite transports moderate quantities of water (several hundred ppm) to mantle depths beyond 100 km, an amount equivalent to that in ca. 1 % calcic amphibole.

Keywords: eclogite, garnet, infrared spectroscopy, nominally anhydrous minerals, omphacite, subduction, water

Introduction

It is known that water plays a key role in mantle dynamics, including convection and magma generation (e.g., Hirth and Kohlstedt 1996; Asimow and Langmuir 2003; Bercovici and Karato 2003). An important question in this context is: How much water is transported into the mantle via subduction? Quartz eclogite typically contains several percent of hydrous minerals, predominantly calcic amphibole and zoisite. However, these minerals are not stable in coesite eclogite and therefore cannot account for the transport of water into mantle regions beyond ca. 100 km. Conversely, water transport to greater depths is possible via nominally anhydrous minerals (NAMs) such as garnet and pyroxene. Both phases, together with olivine, are capable of incorporating considerable amounts of water in their structure (that is, structural hydroxyl or colloquially 'water'; e.g., Bell and Rossman 1992a). Due to the fact that the capacity of these minerals to incorporate water increases with rising pressure (e.g., Kohlstedt et al. 1996; Lu and Keppler 1997), they are crucial for water storage in the mantle.

Garnet and omphacite are the dominant phases in eclogitized oceanic crust and the most important NAMs for subduction-related water transport into the mantle. Two questions arise in this context: (i) How much water is actually stored in coesite eclogite and transported to greater depth, and (ii) are garnet and omphacite able to incorporate the entire water released by the breakdown of eclogite-facies hydrous phases? To seek answers to these questions, NAMs from natural samples of coesite eclogite have to be analyzed for water.

For four reasons, garnet is a very suitable proxy in this context. (i) Garnet is less affected by alteration compared to omphacite. (ii) Omphacite may host nanometer-scale inclusions of various sheet silicates (Schmädicke and Müller 2000; Koch-Müller et al. 2004). (iii) Unlike omphacite, garnet is stable in the transition zone (Ringwood 1991) and is very important for water transport to the deeper mantle. (iv) Its optical isotropy simplifies sample preparation for infrared (IR) spectroscopy – the standard method for measuring water in NAMs (Rossman 2006) – allowing for a larger database.

Several studies have been conducted on ultra-high pressure (UHP) eclogite to determine the water content of garnet, the results, however, are highly variable. Reported garnet water contents of eclogite xenoliths (excluding grospydite and corundum eclogite) fall in a range between zero and 86 ppm (e.g., Bell and Rossman 1992b; see below). Data from massif-type UHP eclogite are available from the Kokchetav Massif and the Dabie-Sulu Orogen. Garnet in Kokchetav coesite eclogite contains 80 - 120 ppm H_2O – concentrations intermediate between those of garnet in quartz eclogite (10 - 50 ppm) and diamond eclogite (130 - 150 ppm; Katayama et al. 2006). In contrast, the water contents of garnet in coesite eclogite from Dabie-Sulu are highly variable ranging from 14 to 1900 ppm (Xia et al. 2005: 90 - 1700 ppm; Sheng et al. 2007: 14 - 1900 ppm; Chen et al. 2007: 18 - 1600 ppm). These results vary by two orders of magnitude even within a single sample or grain, respectively, a fact that can be ascribed to randomly distributed, sub-microscopic fluid inclusions.

Hence, the interpretation of the Dabie-Sulu data basically depends on the origin of the molecular water. In all studies (Xia et al. 2005; Sheng et al. 2007; Chen et al. 2007) an external fluid source was excluded and molecular water in garnet was ascribed to decompressional release of its structural water. Accordingly, molecular water has been interpreted as primary water having been present during peak metamorphism and, therefore, being subject to transport into the mantle beyond 100 km depths.

To evaluate the potential of eclogite for water transport into the mantle, natural, massif-type coesite eclogite – with an assured subduction origin – is the most definitive object to study. The present study of a third massive-type UHP eclogite example was designed to place constraints on (i) the nature of molecular water and (ii) the amount of water carried by subducting eclogite. To this end, four samples of coesite eclogite from the Erzgebirge were selected, and the water content was analyzed in a representative number of garnet grains by IR spectroscopy. This method allows us to distinguish intrinsic or structural hydroxyl in garnet (colloquially water) from water bound in fluid inclusions or hydrous alteration. The water content of the bulk rock can be assessed from the garnet data considering the modal proportions of garnet and omphacite and the H_2O partition coefficient. Because this approach involves some uncertainty, additional data for water in omphacite were obtained by the approach of Kovács et al. (2008) and compared with the estimate based on the published H_2O partition coefficients.

Samples

The investigated coesite eclogite samples are from the Erzgebirge, Germany, which is situated at the northern margin of the Bohemian Massif, the easternmost crystalline complex of the European Variscides. The Erzgebirge is composed mainly of crystalline units; low-grade Palaeozoic sequences occur at the western and northwestern margin (e.g., Schmädicke et al. 1992). The Erzgebirge crystalline complex comprises a medium-pressure unit with quartzofeldspatic gneiss and intercalated amphibolite and three Variscan eclogite-bearing units; one is an UHP unit with coesite eclogite (unit 1) and the other two (units 2 and 3) contain quartz eclogite

(Schmädicke et al. 1992; 1995). The high-pressure units are mainly composed of high-grade quartzofeldspatic gneiss in which eclogite lenses with MORB composition occur as intercalations (Schmädicke 1994). Mantle peridotite is a minor rock type that occurs only in the UHP unit (Schmädicke and Evans 1997). The eclogite-facies peak conditions are 850 - 900 °C and ≥30 kbar in unit 1, 750 °C and 24 - 26 kbar in unit 2, and 650 °C and 20 - 22 kbar in unit 3 (Schmädicke 1991; Schmädicke et al. 1992). Microdiamond inclusions were detected in gneiss in the vicinity of coesite eclogite lenses (Nasdala and Massonne 2000).

Coesite eclogite is characterized by the peak metamorphic assemblage omphacite-garnet-coesite-rutile (decreasing abundance). Unzoned garnet plus omphacite make up 84 - 95 vol% of the rock (Fig. 1). Garnet is an intermediate solid solution with grossular contents of 30±10 mol%; omphacite contains 40±5 mol% jadeite. Prograde mineral inclusions in garnet and omphacite are usually absent – as in all samples studied here; only very rare, exceptional samples contain very few of such inclusions (Schmädicke 1994). Hydrous minerals are not part of the peak assemblage of coesite eclogite, a fact ascribed to physical conditions exceeding their stability field. However, the pre-existence of zoisite, calcic amphibole, and minor phengite in coesite eclogite during an earlier eclogitic stage (i.e., within the stability field of quartz) is inferred from (i) the presence of the three hydrous minerals in all quartz eclogites of units 2 and 3 having the same bulk rock composition as coesite eclogite (Schmädicke 1994), (ii) rare, tiny inclusions in garnet in very few, exceptional samples, and (iii) the fact that garnet in coesite eclogite contains more Ca compared to quartz eclogite. The latter is ascribed to the breakdown of former zoisite enhancing the grossular content in garnet.

Typically, coesite eclogite contains ca. 1 - 2 vol% (rarely up to 5 vol%, as in sample 6) calcic amphibole (pargasitic hornblende) that formed during an early, eclogite-facies decompression stage, presumably in the pressure range of 26 - 30 kbar (Schmädicke et al. 1992). Its interstitial location indicates that amphibole formation post-dates the eclogite-facies peak stage. The low-energy grain boundaries indicate that amphibole re-equilibrated with garnet and omphacite. Inclusions of vermicular quartz (Fig. 1) are a hallmark of this amphibole suggesting that it formed mainly by consumption of omphacite. Such textures are absent in quartz eclogite where amphibole remained stable during peak metamorphism.

Method

Coesite eclogite from four Erzgebirge locations was selected for this study (Table 1). A representative number of garnet grains per sample were analyzed by Fourier transform IR spectroscopy utilizing a Bruker Vertex 70 spectrometer equipped with a Hyperion 3000 microscope and an MCT detector. Doubly polished, self-supporting rock slices were measured with non-polarized IR radiation in transmittance mode. The spectra were obtained by averaging over 32 - 128 scans in the wavenumber range of 550 - 7500 cm^{-1} with an instrumental resolution of 2 cm^{-1}. A square aperture of 30 x 30 to 50 x 50 square micrometers was used to restrict the lateral size of the probed area. Clear and transparent crystal volumes, free of visible inclusions and cracks, were selected for the analysis. Several spectra were collected in a single garnet grain including core and rim areas. The water content was calculated by applying the mineral-specific integral molar absorption coefficient of 6700 L/(mol cm^2) of Bell et al. (1995) that was determined for a garnet with 4.6 wt% CaO, 19.5 wt% FeO, and 11.0 wt% MgO. The integral absorbance was determined by fitting the spectra between 3000 and 3700 cm^{-1}. A polynomial (4th degree) baseline correction was used in order to reproduce the IR spectrum of a heat-treated (1000 °C, 20 hours), dehydrated garnet. A peak-fit software was utilized for the band analysis applying a Gaussian-Lorentzian peak form. The amount of water in the garnet structure (= structural hydroxyl or water, respectively) was determined from absorption bands in the wavenumber range 3490 - 3670 cm^{-1}. In addition, the 'band-specific' water contents (see Results) were determined by using the wavenumber range of 3630 - 3670 cm^{-1} to calculate water related to band type I, and the range of 3490 - 3630 cm^{-1} for band type II, respectively. The content of molecular water, if present, was estimated from absorption bands at wavenumbers <3490 cm^{-1}. With the absorption coefficient of Bell et al. (1995) the amount of molecular water is overestimated by a factor of about two. The same approach was previously used on garnet from eclogite xenoliths (Schmädicke et al. 2015) allowing for better comparison of the garnet water contents from different eclogite types (crustal vs. xenolithic). The major element composition of garnet grains was determined with a JEOL 8200 electron microprobe (Table 1).

In contrast to garnet, the absorption of IR radiation in omphacite, and any other anisotropic mineral, depends on crystal orientation. Therefore, the most precise approach to quantify the water content of a grain of omphacite involves IR analysis with polarized radiation of three randomly oriented but mutually perpendicular crystal directions and two polarizer orientations for each direction as described by Libowitzky and Rossman (1996). However, the preparation of crystals to accomplish such measurements is not always feasible, such as in the case of small grain size or strong fracturing of crystals. Unfortunately, omphacite grains in the four studied eclogite samples are both relatively small and fractured. In such cases, information on the water content can be obtained by an alternative approach that uses measurements of a greater number of crystals by non-polarized radiation as suggested by Kovács et al. (2008) and successfully tested on several minerals, including olivine. The authors have demonstrated that the water contents obtained by their method are identical to the results using the above-mentioned procedure. They also showed that the analysis of ten random grains is sufficient to deduce the average water content for a mineral. Concentration differences between individual grains are more difficult to identify unless they share the same crystal orientation. This, however, is of minor importance in the present context because we are interested in the average water content of omphacite in order to estimate the bulk rock water content for each sample.

To determine the average water content in omphacite of the four eclogite samples we used the same doubly-polished slices as for garnet analysis and measured about 50 individual omphacite grains in each sample slice. The spectra were obtained by averaging over 64 scans. All other details are the same as used for garnet analysis. For each sample, an average spectrum was calculated from all recorded spectra in the wavenumber range of 2600 - 4000 cm^{-1}. The four average spectra were utilized to quantify H_2O for each sample, considering IR absorption in the wavenumber range of 3000 - 3700 cm^{-1}. For background subtraction we used a flat cubic function that fits the water-free sections of the spectra on both sides of the calculated bands. The water contents were calculated utilizing the integral molar absorption coefficient of 38300 L/(mol cm^2) of Bell et al. (1995).

Results

Garnet

Characteristics of IR spectra. All garnet grains contain structural water and most of them additionally host molecular water. The latter is inferred from the broad IR absorption band at 3400 - 3450 cm^{-1} (Fig. 2). This band was ascribed to water in fluid inclusions (e.g., Libowitzky and Beran 1996) and described in almost all previous studies on massif-type UHP eclogite (see below). Two types of IR absorption bands (or band groups) are due to intrinsic water in the garnet structure. Type I is relatively sharp, occurring at 3650 cm^{-1}; type II is broader and has a more variable position in the vicinity of 3600 cm^{-1} (range: 3580 - 3630 cm^{-1}). Type II is most probably related to the hydrogarnet substitution, i.e. H_4O_4 groups replacing SiO_4, and known for changing its position along with garnet composition, including water content, and the resulting local cation configuration (e.g., Geiger et al. 1991; Rossman and Aines 1991). The band type I was ascribed to water incorporation via tetrahedral [$SiO_3(OH)$] groups charge balanced by cation vacancies on dodecahedral (Lu and Keppler 1997) or dodecahedral and octahedral sites (Andrut et al. 2002).

Water content. All four samples studied are characterized by strongly varying IR band intensities, even on grain scale, but a systematic difference between garnet cores and rims is not observed. Band type I is present in all eclogite samples and in every analyzed garnet grain or grain volume, respectively. The band has roughly constant intensity comparing different garnet grains of a single eclogite sample or different grain volumes (e.g., core and rim domains) of a single garnet grain, respectively. Intensity differences of band type I between the four eclogite samples are minor to moderate (Fig. 2). In contrast, the intensity of band type II is highly variable. The band intensity and the water content ascribed to this band may vary up to one order of magnitude (Fig. 2; Table 2).

As a result, the water contents of garnets from all four eclogite samples vary over a large range, but the difference between the four eclogites is relatively small. The variability is greatest if intrinsic (revealed by band types I + II) and molecular water are added. Total water contents range over two orders of magnitude from tens to more than 1000 ppm (maximum ranges: 16 - 1273 ppm in sample 4 and 64 - 1508 ppm in sample Vo; Table 2). This scatter reflects the irregular distribution of molecular water (fluid inclusions) not only between different garnet grains in a sample but also within a single grain (Fig. 3). Nevertheless, even if molecular water is neglected, the contents of intrinsic (structural) water, determined by summing the water contents attributed to band types I and II, still vary over one order of magnitude in a single sample and even in a single grain, from tens to several hundred ppm (maximum: 63 - 717 ppm in sample Vo; Table 2; Fig. 4).

Comparing the arithmetic mean of structural water in the samples (sample 4: 120 ppm, sample 6: 133 ppm, sample 10.3: 78 ppm, sample Vo: 228 pm; Table 2) and the mode (the most frequent concentration) inferred from the histograms (sample 4: 55±10 ppm, sample 6: 95±10, sample 10.3: 65±10 ppm, sample Vo: 95±10 ppm; Fig. 4), the latter is always lower. However, considering only garnet volumes that are free of molecular water, the contents of intrinsic water are much more consistent and cover a maximum range of 16 - 105 ppm for the entire data set (in contrast to 16 - 1508 ppm including all garnet volumes; Table 2). The range of sample averages is even smaller: 43 ppm (sample 4), 58 ppm (sample 10.3), and 84 ppm (samples 6 and Vo). Notably, these contents agree exceptionally well with the above given modes.

Most importantly, the IR spectra (Fig. 2) reveal that the intensity of the type II band positively correlates with the presence and intensity of the molecular water band. Moreover, in spectra without molecular water, the type II band is very small or even virtually absent. This also becomes obvious if the water contents attributed to band type II or band type I, respectively, are plotted against the amount of molecular water (Fig. 5). All four samples show a pronounced positive correlation between water due to type II bands and molecular water with correlation coefficients of 0.92 (sample 4), 0.97 (sample 6), 0.93 (sample 10.3), and 0.96 (sample

Vo), whereas water ascribed to type I bands is not correlated to molecular water (samples 4 and 10.3 with coefficients of 0.30 and 0.25, respectively) or more weakly correlated (samples 6 and Vo with correlation coefficients of 0.75 and 0.82, respectively) than type II bands.

Omphacite

The IR spectra of omphacite reveal three prominent bands that are present in all samples (Fig. 6, Table 3). The strongest band occurs at ca. 3450 - 3460 cm^{-1}, the second strongest at 3520 - 3530 cm^{-1}, and the third, small band at 3620 cm^{-1}. All three bands were previously described from omphacite (e.g., Koch-Müller et al. 2004; Sheng et al. 2007) and are attributed here to structural water. The estimated water content for omphacite, using the contribution of all three bands, is in the range of 400 - 820 ppm, depending on the sample (Table 3). It cannot be excluded that omphacite additionally contains molecular because, if present, the indicative band would be obscured by the prominent structural water band at 3450 - 3460 cm^{-1}. However, judging from the spectra and the relative contribution of the three bands to the overall water content, the amount of molecular water, if present, should be relatively small (compared to garnet). It should be mentioned that Koch-Müller et al. (2004) attributed the band around 3620 cm^{-1} to sheet silicate inclusions in omphacite. If true, the content of structural water given in Table 3 is overestimated. The presence of such inclusions in our sample is not unlikely. In fact, lamellar sheet silicate inclusions in omphacite were detected in another sample of Erzgebirge coesite eclogite by transmission electron microscopy (Schmädicke and Müller 2000). In addition, two of the omphacite samples (10.3 and Vo) investigated here show very fine, parallel lamellae of an unidentified phase in thin section. If these lamellae also consist of sheet silicates or were formed by quartz exsolution (Schmädicke et al. 1992) can only be disclosed by electron microscopy. Despite of this ambiguity, the contribution of the questionable band (that might stem from a sheet silicate) to the overall water content is relatively small (≤10 %).

Discussion

Comparison with previous studies

Previous studies on the water content of garnet in UHP eclogite include both eclogite xenoliths and samples from massif-type eclogite occurrences. Reported garnet water contents of eclogite xenoliths (excluding grospydite and corundum eclogite) fall in a range between zero and 86 ppm (Bell and Rossman 1992b: 0 - 86 ppm; Snyder et al. 1995: 0 - 72 ppm; Matsyuk et al. 1998: <4 ppm; Schmädicke et al. 2015: 2 - 13 ppm). The highest concentrations measured by Bell and Rossman (1992b) and Snyder et al. (1995), respectively, are not typical for their datasets; the majority of values are ≤20 ppm. This agrees with the data from the other studies (Matsyuk et al. 1998; Schmädicke et al. 2015) indicating a range of 0 - 20 ppm H_2O to be typical for garnet from xenolithic UHP eclogite. Surprisingly, water concentrations in diamond eclogite are as low as <5 ppm (e.g., Peslier 2010). This result is not in conflict with the reported pressure-enhanced water storage capacity (e.g., Lu and Keppler 1997) but may simply reflect the low water fugacity in the mantle source (Peslier 2010).

Data from massif-type UHP eclogite are available from two occurrences. Garnet in coesite eclogite from the Kokchetav Massif contains 80 - 120 ppm H_2O. Lower concentrations were reported from garnet of Kokchetav quartz eclogite (10 - 50 ppm) and higher ones from garnet in diamond eclogite (130 - 150 ppm; Katayama et al. 2006). In contrast, garnet in coesite eclogite from the Dabie-Sulu orogen has more variable and, on average, much higher water contents. The concentrations range from 14 to 1900 ppm (Xia et al. 2005: 90 - 1700 ppm; Sheng et al. 2007: 14 - 1900 ppm; Chen et al. 2007: 18 - 1600 ppm) and vary by two orders of magnitude even within a single sample or grain, respectively. This observation can be attributed to sub-microscopic fluid inclusions. In fact, clusters of 0.06 mm sized fluid inclusions with water molecules were observed by electron microscopy (Su et al. 2002). The presence of molecular water in most published IR spectra (Xia et al. 2005; Sheng et al. 2007; Chen et al. 2007) can additionally be inferred from the characteristic absorption band at ca. 3400 cm^{-1}. By inspecting the published spectra it becomes obvious that the majority of the reported H_2O contents represent fluid inclusions and not structural water, thus explaining the extremely high concentrations and the large scatter in the datasets.

Comparing the results from previous studies, the water contents of garnet in coesite eclogite from Kokchetav are higher than the average data for eclogite xenoliths but overlap with the highest contents recorded in the latter. The lowest contents reported from massive-type Dabie-Sulu eclogite (14-90 ppm) are also compatible with the other results, but most data are at least one order of magnitude higher (due to molecular water).

The primary water contents in garnet of 43 - 95 ppm (see below) determined in this study closely resemble those from other massif-type and xenolithic UHP eclogites. They are similar to the data of Kokchetav coesite eclogite (80 - 120 ppm; Katayama et al. 2006) and coincide with the highest contents reported from eclogite xenoliths (86 ppm; Bell and Rossman 1992b).

The same applies to omphacite. Reported water contents in xenolithic samples are in the range of 61 - 790 ppm (Koch-Müller et al. 2004). Again, the highest contents of xenolithic omphacite overlap with the results from this study (400 - 820 ppm). Sheng et al. (2007) determined similar concentrations of 115 - 695 ppm for omphacite from massif-type UHP eclogite (Dabie-Sulu). In contrast, higher concentrations of up to 3000 ppm were recorded for Kokchetav omphacite (Katayama and Nakashima 2003), but it is not clear whether these contents are partly due to hydrous phase inclusions as Koch-Müller et al. (2004) suggested.

Is molecular water primary or secondary?

The key question resulting from this and former studies concerns the nature of molecular water in garnet. Possibility I: As suggested previously (see Introduction), decompressional release of structural water in garnet led to fluid inclusions with molecular water. If true, molecular water has to be treated as primary and added to the content of structural water. In this case, a large amount of water (up to nearly 1 wt%) results for the bulk rock that would potentially be transported by eclogite to greater depths. Possibility II: Molecular water is secondary and attributed to post-peak metamorphic fluid influx. In this case, the amount of water being subject to transport into the deeper mantle is at least one order of magnitude smaller. For four reasons, the results of the present study support the latter possibility:

1. Molecular water is irregularly distributed in a sample. The amount of molecular water strongly varies not only between different garnet grains in a sample but also within a single grain (Fig. 3). Most importantly, there is evidence of garnet grains that are free of molecular water whereas other grains in the same sample (only a few millimeters apart) contain plenty of it (Fig. 3). These observations can hardly be reconciled with a model explaining molecular water as former structural water.

2. If molecular water in garnet were primary, unrealistically high water contents in coexisting omphacite would result under equilibrium conditions that are in contrast to the concentrations actually measured in omphacite. This reasoning is based on published data for garnet-omphacite H_2O partition that can be used in this context. For natural coesite eclogite a coefficient of 0.1 - 0.2 was determined (Katayama et al. 2006). Bell et al. (2004) demonstrated that the partition coefficient for garnet-clinopyroxene pairs decreases with increasing Fe content and determined a coefficient of 0.2 for the sample with the highest Fe content (Mg# 0.68 - 0.70). Since crustal eclogite, including the Erzgebirge occurrences, is typically more Fe-rich (Mg# ≤ 0.5; Schmädicke 1994), the coefficient should be < 0.2 in such samples, and this value well agrees with the estimate of the present study (see below and Table 4). If molecular water is added to the content of structural water in garnet, average water contents of 127 - 454 ppm and maximum contents of 488 - 1508 ppm would result, depending on the sample (Table 2). Utilizing these data and a garnet-omphacite H_2O partition coefficient of 0.1, the water content of coexisting omphacite calculates to 1270 - 4540 ppm (average values) and 4880 - 15080 ppm (maximum values). Such contents by far exceed both the so-far known experimentally predicted H_2O storage capacity of jadeitic pyroxene (e.g., Bromiley and Keppler 2004) and the maximum concentrations of natural samples (e.g., Koch-Müller et al. 2004; Skogby 2006; Sheng et al. 2007; Peslier 2010). In fact, the maximum amount of 15080 ppm H_2O for sample Vo is a typical content for amphibole but

not pyroxene. Hence, the water contents measured in omphacite together with the so-far known garnet-omphacite partition coefficients cannot be reconciled with the garnet data if molecular water is included and regarded as primary.

3. Equally important is the above-mentioned fact that the intensity of structural water bands of type II correlates positively with the amount of molecular water (Figs. 2, 3, and 5). If molecular water really originated from released structural water that was homogeneously distributed on grain scale, a negative correlation (or no correlation at all) would be expected but definitely not the observed positive trend.

4. The structural water band of type I behaves differently than the type II band in relation to molecular water (Fig. 5). The intensity of the type I band is not related to the presence nor the amount of molecular water in half of the samples and weakly correlated in the other half, whereas type II bands show a clear positive correlation in all samples. The band type I is probably related to tetrahedral water incorporation in the form of [$SiO_3(OH)$] groups charge balanced by cation vacancies on dodecahedral and/or octahedral sites (Lu and Keppler 1997; Andrut et al. 2002), whereas type II bands are ascribed to the tetrahedral hydrogarnet substitution (e.g., Geiger et al. 1991; Rossman and Aines 1991). Experiments by Lu and Keppler (1997) have demonstrated that the two bands respond remarkably different to pressure. While the total H_2O content increases with pressure, only band type I grows in intensity while type II shrinks. This opposite pressure dependence is ascribed to the fact that the hydrogarnet substitution is not favored by high pressure because of the increasing lattice volume related to the substitution (Lu and Keppler 1997). These results from high-pressure experiments can perfectly be reconciled with the findings of the present study. The observation that type II and molecular water bands, and the corresponding water species, are correlated points to a genetic relation. The most plausible explanation is that both formed during decompression as a result of water influx giving rise to fluid inclusions. Apparently, water in fluid inclusions enhanced the content of structural water (type II) in garnet volumes close to such inclusions. A similar observation was made for garnet and plagioclase from re-hydrated granulite (Németh et al. 2015). Admittedly, our interpretation for the Erzgebirge samples

does not necessarily apply to all cases. It is also possible that hydrous fluid inclusions result from decompressional release of structural water, as suggested for Dabie-Sulu eclogite (Xia et al. 2005).

In conclusion, decompressional release of structural water cannot serve as the source of molecular water in the studied Erzgebirge eclogites. Moreover, the increasing intensity of the hydrogarnet band (type II) along with the amount of molecular water strongly suggests that both are related to decompression. We conclude that both molecular water and water bound by the hydrogarnet substitution are secondary (post-peak metamorphic) and do not reflect UHP peak conditions. This does not exclude their formation at eclogite-facies conditions. In fact, post-peak fluid influx is most likely attributed to an early, eclogite-facies decompression stage. This is because growth of amphibole with vermicular quartz (Fig. 1) but not of zoisite provides independent evidence for post-peak fluid influx at 26 - 30 kbar.

Admittedly, the growth of amphibole, or any hydrous phase, is not a universal proof of fluid influx, and alternatives have to be taken into account. In fact, amphibole may grow in ultra-high pressure rocks during decompression simply by re-entering its stability field at $P \leq 30$ kbar (Schmädicke 2000), provided some grain-boundary fluid or other internal fluid is available. Likewise, the onset of retrograde overprint in metamorphic rocks has also been linked to decompressional release of structural water from nominally anhydrous minerals (e.g., Peslier 2010). In the present case, the contents of calcic amphibole range from 1 - 2 to 5 vol%. This corresponds to bulk rock water contents (bound to amphibole) ranging from 200 - 400 to 1000 ppm. This amount, if interpreted in terms of decompressional release of structural water from garnet and omphacite, has to be added to the quantity measured in both minerals to decipher the original water content of eclogite. Adding the amphibole water to the contents recorded by garnet and omphacite (indicating 280 - 460 ppm for the bulk rock; see below), the original water contents of the bulk eclogite would be about 500 - 1500 ppm. This concentration, if stored in garnet and omphacite, translates into maximum H_2O contents of 2060 - 2660 ppm in omphacite, exceeding its experimentally determined water storage capacity (see below). In conclusion, we interpret the formation of calcic amphibole in Erzgebirge coesite eclogite in terms of fluid infiltration and ascribe the numerous inclusions of molecular water in garnet to the same event of fluid influx.

What is the primary garnet and bulk rock water content?

Our results suggest that fluid influx during decompression led to fluid inclusions, being inhomogeneously distributed on grain scale. As a result, garnet incorporated additional structural water via the hydrogarnet substitution in close vicinity to fluid inclusions due to locally enhanced water fugacity. Previously present intrinsic water, predominantly bound by other substitutions, is not influenced in samples 4 and 10.3 and possibly moderately enhanced in samples 6 and Vo.

Hence, the primary, peak metamorphic water content of garnet is preserved only in crystal volumes that are free of molecular water. These volumes include little or no water bound via the hydrogarnet substitution. The average H_2O contents in such domains are 43 ppm (sample 4), 58 ppm (sample 10.3), and 84 ppm (samples 6, Vo), being considerably lower than in secondarily hydrated volumes (Table 2). Notably, those average water contents are very close, or identical, to the mode (the most abundant concentration) of each sample (Fig. 4): 55±10 ppm (sample 4), 65±10 ppm (sample 10.3), and 95±10 ppm (samples 6, Vo). This agreement suggests that both approaches are suitable to infer the primary water content of garnet.

Based on the inferred primary water content of garnet and the concentration measured in omphacite, an H_2O content of 280 – 460 ppm can be estimated for the bulk eclogite (Table 4). Judging from the data for Erzgebirge eclogite determined in this study, an average garnet-omphacite H_2O partition coefficient of 0.12 (range 0.07 - 0.18) is derived (Table 4). This result coincides with the values previously published by Bell et al. (2004) and Katayama et al. (2006).

Before evaluating the water amount that is potentially transported to greater depths by subducting UHP eclogite, the problem of water loss needs to be addressed. In other words, are the primary water contents inferred here identical to the original ones at the time of UHP peak metamorphism? To shed light on this issue, the water contents determined here first need to be compared with literature data. As discussed above, the water contents of garnet and omphacite determined in this study compare well with those from other massif-type UHP eclogites and also overlap with the highest contents obtained in xenolithic samples. On average, there is a shift to somewhat higher water contents in omphacite from massif-type samples compared to xenoliths (Peslier 2010) but the reason behind this is not clear. This finding is supported by our study and applies to both garnet and omphacite. Variable water fugacity during UHP equilibration in the different settings is one possibility to explain the observed trend. It is also conceivable that the difference is due to the silica activity, being lower for part of eclogite xenoliths compared to massif-type equivalents. This, at least, applies to clinopyroxene (e.g., Karimova and Stalder 2013). Another explanation could be a greater tendency to decompressional water loss in the case of xenolithic samples (see below).

To discriminate between the possible options, knowledge of the water storage capacity of garnet and omphacite is needed. Experimental data show that the storage capacity of natural pyropic garnet (containing about 5 mol% 'impurities') at 30 kbar is 50 ppm (Lu and Keppler 1997). Though this value is close to the primary water contents measured in Erzgebirge garnet, it is unlikely that it corresponds to the maximum amount of storable water, simply because the Erzgebirge garnet is compositionally different. Particularly, the latter contains more Ca, and Ca-rich garnet is able to incorporate more water in its structure. For instance, garnet from UHP calc-silicate rocks was reported to host 180 - 690 ppm water (Langer et al. 1993) and garnet in grospydite contains 620 ppm (Beran et al. 1993). In these rocks, however, garnet is extraordinarily rich in grossular component (50 mol%), again not matching the composition of Erzgebirge garnet. Thus, without the knowledge of the water storage capacity for a specific garnet composition, it is not clear if the high water content in garnet of calc-silicate rocks and grospydite is governed by its grossular-rich composition or is simply due to higher water fugacity in such lithologies. The situation for omphacite is similar. Experiments yielded 460 ppm water in jadeite-diopside solid solutions at a pressure of 25 kbar, and 780 ppm in jadeite-Ca-Eskolaite pyroxene at 20 kbar (Bromiley and Keppler 2004). The latter value well agrees with the results of this study. Nonetheless, the storage capacity in the present case may, again, be different because the composition of natural omphacite, also containing Fe, Ti, and further minor and trace elements, is more complex.

Even though the water storage capacity for mineral compositions close to those of our samples is unknown, we infer that the Erzgebirge samples do not contain the maximum possible amount of water. This is deduced from the fact that garnet, in addition to primary water, incorporated secondary structural water by diffusion from fluid inclusions. Uptake of water in a mineral's structure is only feasible in the case that it is H_2O under-saturated – having the capacity to store additional water. Hence, the water concentrations referred here as primary correspond, in all likelihood, to under-saturated conditions. If these contents mirror the original state at the UHP peak or resulted from decompressional water loss is another matter that has to be evaluated. Judging from the presently available data, we infer that water loss was insignificant or did not occur at all.

First, diffusional water loss cannot be reconciled with the observed distribution of water in single garnet grains. There is no indication of lower contents at the rim, let alone of diffusional profiles as described by Peslier and Luhr (2006). Owing to the high diffusivity of hydrogen in garnet (e.g., Blanchard and Ingrin 2004), one might argue that diffusion profiles are easily obliterated resulting in a homogeneous distribution of water in a mineral grain. However, this cannot be reconciled with the present investigation demonstrating that garnet preserved highly variable water contents on grain scale and implying that diffusional re-homogenization was strongly limited.

Second, experiments on natural pyrope with IR bands identical to those in our samples, revealed that the type I band decreases at least five times faster than the type II band during dehydration (Blanchard and Ingrin 2004). However, the garnet domains in our samples defined as primary (i.e., those without molecular water) are dominated by the type I band whereas a type II band is minor or absent. However, water loss should cause the opposite (smaller or lacking type I bands).

Third, it is difficult to explain that garnet first lost water in response to decompression and, later on, incorporated additional water under conditions that were even less favorable (lower *P* and *T*) compared to those at which water loss should have occurred.

Hence, the conclusion that the low water contents are primary and did not result from water loss can be reconciled best with all observations made in the present study. Nonetheless, this result is surprising because the slow tectonic exhumation of massif-type eclogite should provide for more extensive water loss compared to rapidly uplifted eclogite xenoliths. Possibly, the decompression-cooling path is more important in this context than previously considered. Water loss seems to be more restricted or absent if decompression is accompanied by cooling (Schmädicke et al. 2011) in contrast to isothermal decompression that is typical for xenoliths (Peslier and Luhr 2006). The fact that massif-type eclogites, including the Erzgebirge examples (Schmädicke et al. 1992), cooled during exhumation may explain why they preserve higher average water contents than eclogite xenoliths. Moreover, massif-type eclogites typically record lower peak temperatures (≤900 °C) than xenoliths (≥1000 °C). Since the former progressively cool during exhumation, their average exhumation temperature is several hundred degrees lower compared to that of xenoliths.

In conclusion, our examples of Erzgebirge UHP eclogite point to moderate amounts of water, on the order of several hundred ppm (280 - 460 ppm, determined here), being subject to transport to mantle depths beyond 100 km. Furthermore, the NAMs in the investigated examples of UHP eclogite presumably were not water-saturated at peak metamorphism. Though the water contents of garnet and omphacite coincide with the experimentally established water storage capacities of these minerals, at least garnet was capable to incorporate secondary structural water during exhumation, which is only possible if the mineral previously hosted less water than it is able to accommodate in its structure.

Implications: What is the fate of water from dehydration reactions and the source of water for re-hydration in eclogite?

The inferred peak metamorphic H_2O content of coesite eclogite stored in NAMs (280 - 460 ppm; Table 4) is much lower compared to the amount generated by prograde, eclogite-facies dehydration reactions. Using Erzgebirge quartz eclogite from unit 2 as a template, ca. 2.5 - 5 % of each zoisite and calcic amphibole were stable at peak metamorphism. If such rocks are subducted further and reach UHP conditions, both phases decompose and together release ca. 1500 - 3000 ppm H_2O. This exceeds the peak-metamorphic amount stored in NAMs of Erzgebirge coesite eclogite by one order of magnitude. Obviously, the greatest part of the water generated by dehydration reactions during the transition from HP to UHP conditions was liberated and presumably escaped to the hanging wall. Our finding agrees well with the suggestions of Dixon et al. (2002) that water is extracted from subducting oceanic crust with an efficiency of 97 % and that accumulation of dehydrated oceanic crust in the mantle results in relatively dry mantle components ('HIMU' with ca. 600 ppm H_2O).

Accordingly, we ascribe secondary water for re-hydration of Erzgebirge UHP eclogite – causing fluid inclusions, hydrogarnet substitution, and growth of eclogite-facies, post-UHP amphibole – to the breakdown of hydrous phases in subducting eclogite in the footwall of the exhuming UHP unit. A similar model suggested by Konrad-Schmolke et al. (2011) links pervasive fluid influx and retrogression in exhuming eclogite to dehydration in subducting slabs in the footwall. We finally conclude that retrogression and hydrous phase formation in eclogite basically depends on fluid influx from an external source. The alternative – attributing water for retrogression to decompressional release of structural water from NAMs can only play a minor, if any, role in the investigated samples of Erzgebirge coesite eclogite.

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Figure captions

Figure 1. Photomicrograph of Erzgebirge coesite eclogite. (a), (b): sample Vo; (c), (d): sample 10.3. Garnet and omphacite are cut by late fractures. Interstitial calcic amphibole (central, brown-colored grain) is a typical minor phase (1 - 5 vol%). Not being stable under UHP conditions, amphibole in coesite eclogite formed during an early, eclogite-facies decompression stage at 26 - 30 kbar and re-equilibrated with garnet and omphacite. This post-peak metamorphic amphibole is anhedral and invariably hosts inclusions of vermicular quartz. The latter suggest that amphibole grew mainly by consuming omphacite. (a), (c) taken with plane polarized light; (b), (d) taken with crossed polars.

Figure 2. IR absorption spectra of garnet grains from four coesite eclogite samples, normalized to 1 cm sample thickness. Up to three types of absorption bands occur: Types I (at 3650 cm^{-1}) and II (at 3580 - 3630 cm^{-1}) are caused by intrinsic water in the garnet structure. The third, broad band (centered at 3400 - 3450 cm^{-1}) is indicative of molecular water in fluid inclusions. Note that the intensity of the latter correlates with that of type II bands. See text for further information.

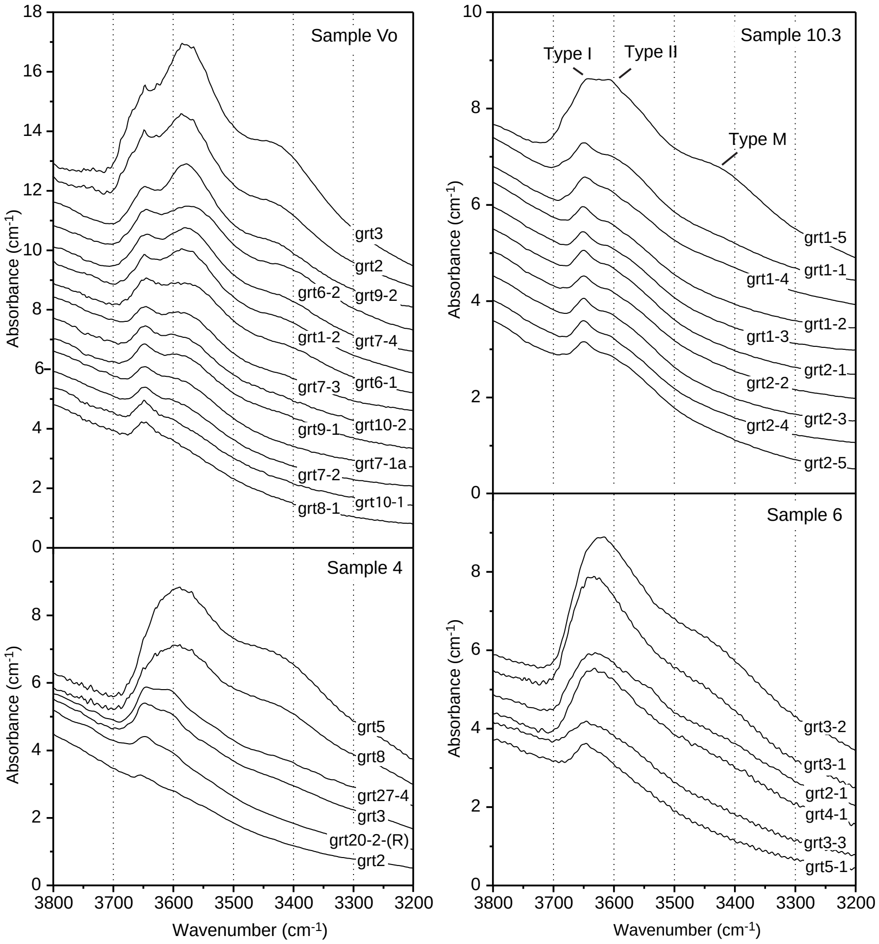
Figure 3. Back-scattered electron images of garnet showing the spatial distribution of water. The numbers above the line give the amount of structural water according to band type I (first number) and band type II (second number). The number below the line refers to the amount of molecular water. Note that the content of structural water due to band type II is higher in domains with molecular water. (a) Garnet grain 1 of eclogite sample 10.3 with variable amounts of structural and molecular water. This pattern is typical for all samples and most investigated grains. (b) Exceptional grain 2 of sample 10.3 in which molecular water is virtually absent.

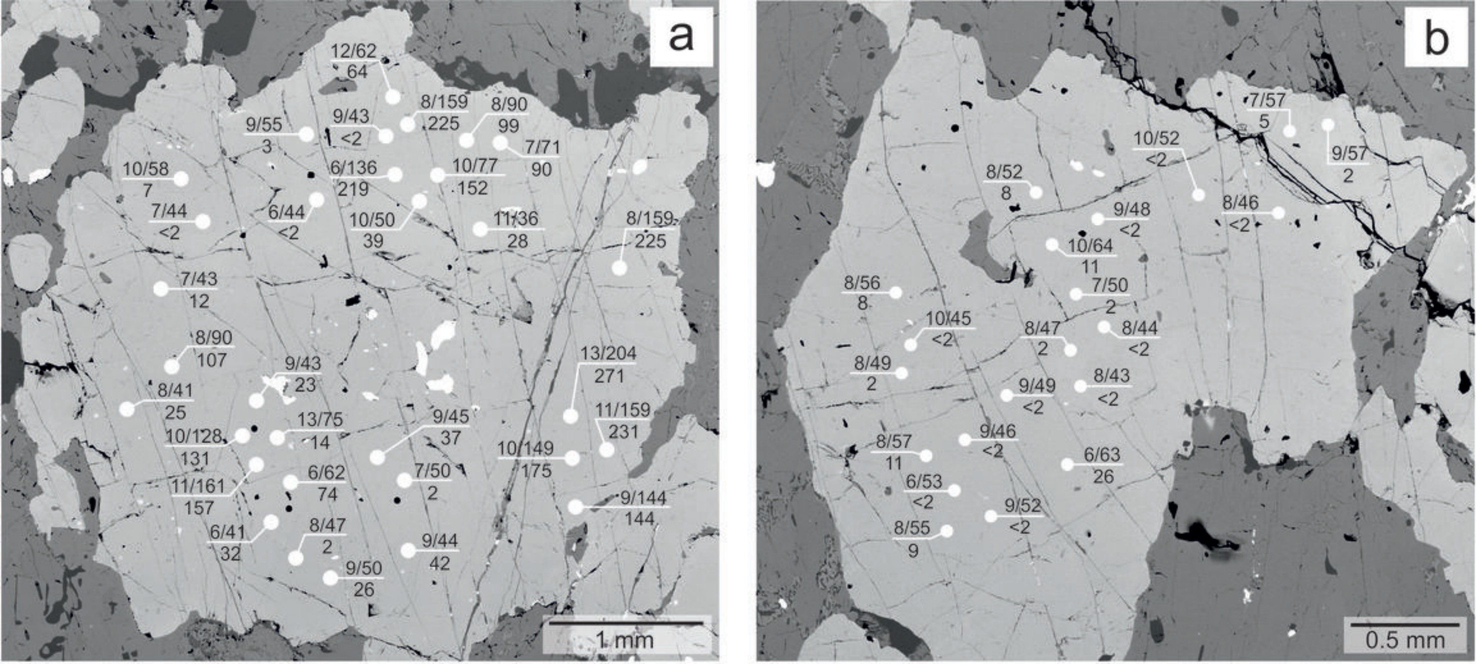
Figure 4. Histograms illustrating the distribution and content of structural water in garnet from coesite eclogite. The values represent the sum of water due to band types I and II in individual garnet grains. The considerable spread of individual values is attributed to the influence of molecular water. Despite of this variability, the mode is ≤100 ppm in all four samples (sample 4: 55±10 ppm, sample 6: 95±10 ppm, sample 10.3: 65±10 ppm, and sample Vo: 95±10 ppm). The modes are basically identical to the content of primary structural water inferred from domains without inclusions of molecular water (sample 4: 43 ppm, sample 6: 84 ppm, sample 10.3: 58 ppm, and sample Vo: 84 ppm; Table 2).

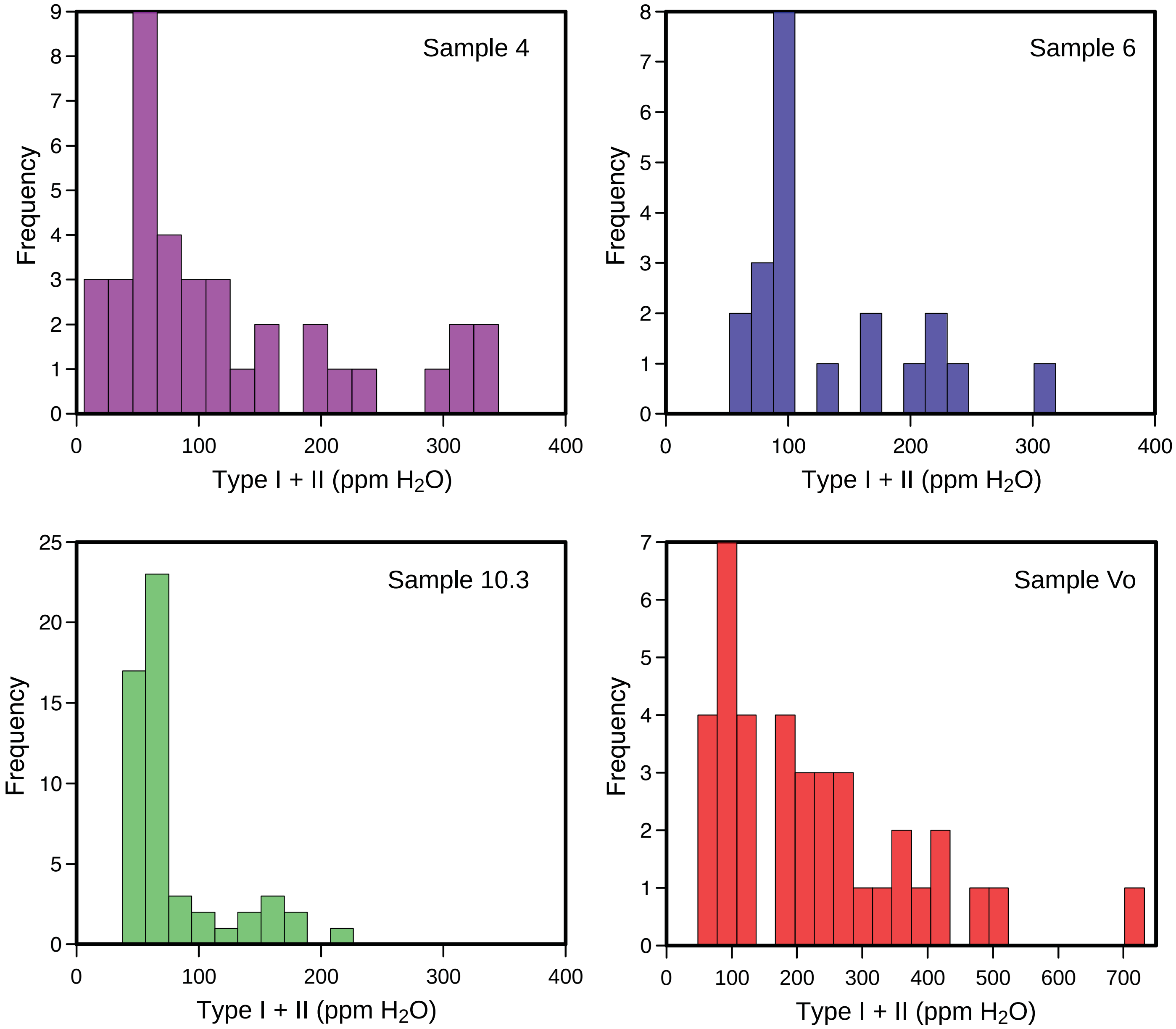
Figure 5. Contents of structural water due to band type I or band type II, respectively, plotted against the amount of molecular water (type M). The water content due to band type II positively correlates with the amount of molecular water. In contrast, for band type I such a correlation is absent (samples 4 and 10.1) or less pronounced (samples 6 and Vo) compared to type I bands.

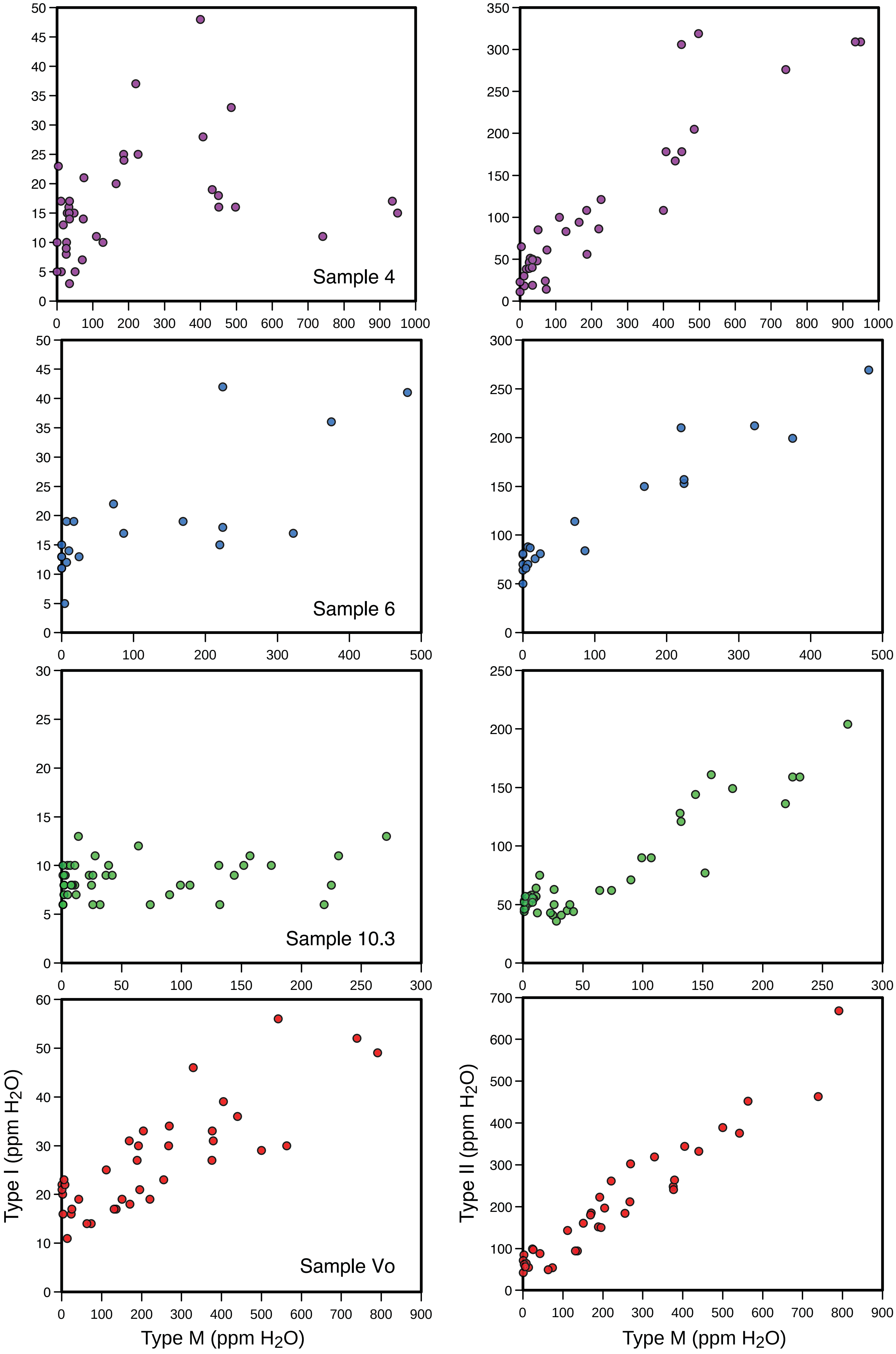
Figure 6. IR absorption spectra of omphacite, normalized to 1 cm sample thickness. The spectra reflect the average absorption for each sample, calculated from the spectra of about 50 different omphacite grains.


a
Grt
Qtz
Amph
Om
Om
Om
0.2 mm
b
c
Om
Grt
Amph
Om
d


Sample Vo
grt3
grt2
grt9-2
grt6-2
grt7-4
grt1-2
grt6-1
grt7-3
grt10-2
grt9-1
grt7-1a
grt7-2
grt10-1
grt8-1
Sample 4
grt5
grt8
grt27-4
grt3
grt20-2-(R)
grt2
Sample 10.3
Type I
Type II
Type M
grt1-5
grt1-1
grt1-4
grt1-2
grt1-3
grt2-1
grt2-2
grt2-3
grt2-4
grt2-5
Sample 6
grt3-2
grt3-1
grt2-1
grt4-1
grt3-3
grt5-1
Absorbance (cm-1)
Wavenumber (cm-1)
0
2
4
6
8
10
12
14
16
18
3800
3700
3600
3500
3400
3300
3200


a
12/62
64
8/159
225
8/90
99
9/55
3
9/43
<2
7/71
90
10/58
7
6/136
219
10/77
152
7/44
<2
6/44
<2
10/50
39
11/36
28
8/159
225
7/43
12
8/90
107
13/204
271
9/43
23
8/41
25
11/159
231
13/75
14
9/45
37
10/128
131
10/149
175
6/62
74
7/50
2
11/161
157
9/144
144
6/41
32
8/47
2
9/44
42
9/50
26
1 mm
b
7/57
5
10/52
<2
9/57
2
8/52
8
8/46
<2
9/48
<2
10/64
11
8/56
8
7/50
2
10/45
<2
8/47
2
8/44
<2
8/49
2
8/43
<2
9/49
<2
9/46
<2
8/57
11
6/63
26
6/53
<2
9/52
<2
8/55
9
0.5 mm


Sample 4
Frequency
0
1
2
3
4
5
6
7
8
9
0
100
200
300
400
Type I + II (ppm H_2O)
Sample 6
Frequency
0
1
2
3
4
5
6
7
8
0
100
200
300
400
Type I + II (ppm H_2O)
Sample 10.3
Frequency
0
5
10
15
20
25
0
100
200
300
400
Type I + II (ppm H_2O)
Sample Vo
Frequency
0
1
2
3
4
5
6
7
0
100
200
300
400
500
600
700
Type I + II (ppm H_2O)


Sample 4
Sample 6
Sample 10.3
Sample Vo
Type I (ppm H_2O)
Type II (ppm H_2O)
Type M (ppm H_2O)
Type M (ppm H_2O)

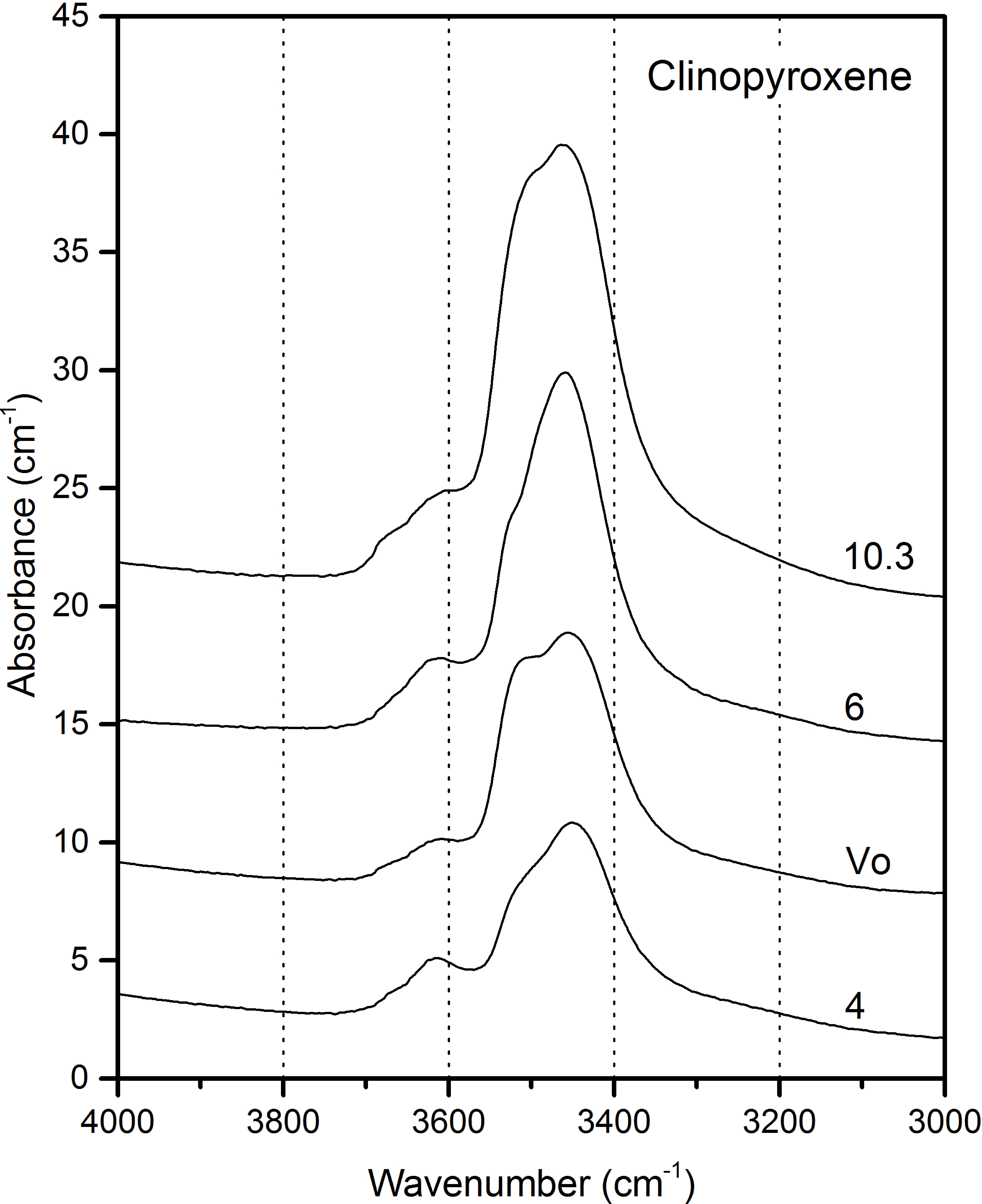

Clinopyroxene
10.3
6
Vo
4
Absorbance (cm^{-1})
Wavenumber (cm^{-1})
0
5
10
15
20
25
30
35
40
45
4000
3800
3600
3400
3200
3000

Table 1. Modal contents (vol%) and garnet composition (mol%) of the investigated Erzgebirge coesite eclogites. Hornblende is not part of the peak assemblage but formed during a late-eclogitic stage, and symplectite (clinopyroxene + plagioclase) is post-eclogitic. The major garnet endmembers are grossular (grs), almandine (alm), and pyrope (pyr); minor components such as spessartine are not given. + = present as trace, - = not present.

Sample	Garnet	Omphacite	Coesite/ Quartz	Rutile	Horn- blende	Symplec- tite	Opaque phases	Composition grs-alm-pyr
4	30	60	5-10	1	1	<1	+	23-49-27
6	30	54	5	2	5	2	2	38-39-21
10.3	45	50	2	<1	1	1	+	34-32-32
Vo	30	62	5	1-2	1	-	<1	29-44-26

Table 2. Water content in garnet of Erzgebirge coesite eclogite. Almost all garnet grains host structural (SW) and molecular water (MW). The latter is bound to irregularly distributed fluid inclusions. The primary content of structural water is deduced from garnet volumes that are free of molecular water. Avg = average, N = number of quantified spectra.

Sample (N)	SW + MW Avg (range) H_2O [ppm]	SW Type I Avg (range) H_2O [ppm]	SW Type II Avg (range) H_2O [ppm]	SW total Avg (range) H_2O [ppm]	Primary SW Avg (range) H_2O [ppm]
4 (37)	325 (16-1273)	17 (3-48)	103 (11-319)	120 (16-335)	43 (16- 88)
6 (21)	240 (61- 791)	18 (5-42)	115 (50-269)	133 (61-310)	84 (61-101)
10.3 (54)	127 (51- 488)	9 (6-13)	70 (36-204)	78 (47-217)	58 (47- 68)
Vo (37)	454 (64-1508)	27 (11-56)	201 (42-668)	228 (63-717)	84 (63-105)

Table 3. Water content in omphacite of Erzgebirge coesite eclogite calculated from the average spectra in Fig. 6. N = number of recorded spectra, + = visible in thin section, - = not visible in thin section.

Sample (N)	Main IR bands [cm^{-1}]	Average integrated absorbance [cm^{-2}]	H_2O [ppm]	Lamellar inclusions
4 (56)	3450, 3520, 3620	2819	400	-
6 (56)	3454, 3521, 3620	4187	590	-
10.3 (45)	3462, 3529, 3620	5757	820	+
Vo (49)	3458, 3522, 3620	3343	470	+

Table 4. Primary content of structural water (SW) in garnet (see Table 2), total content of SW in coexisting omphacite (om) and calculated H_2O content for the bulk eclogite utilizing the modal proportions given in Table 1 and ignoring possible contributions of minor primary phases such as rutile and coesite/quartz.

Sample	Grt H_2O [ppm] Primary SW	Om H_2O [ppm] Total SW	K_D Grt/Om	Eclogite H_2O [ppm]
4	43	400	0.11	281
6	84	590	0.14	409
10.3	58	820	0.07	459
Vo	84	470	0.18	344