Nature of hydrogen defects in clinopyroxenes from room temperature up to 1000 °C: Implication for the preservation of hydrogen in the upper mantle and impact on electrical conductivity

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Revision 2

Nature of hydrogen defects in clinopyroxenes from room temperature up to 1000 ^{o}C: Implication for the preservation of hydrogen in the upper mantle and impact on electrical conductivity

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ABSTRACT

Water incorporated as hydrogenated defects in mantle minerals can influence physical properties of the mantle. Knowledge of hydrogen defects at high temperatures (*T*) is fundamental to understand and quantify their influence on mantle physical properties. Clinopyroxene contributes significantly to the upper mantle water budget. Here, we investigate the behavior of hydrogen defects in ten natural clinopyroxene crystals at temperatures up to 1000 ^{o}C, using *in situ* and quenched experiments. The *in situ* high *T* Fourier transform infrared (FTIR) spectra indicate no proton transfer between point defects, but the local environments of hydrogen defects vary. Dehydration rates at 1000 ^{o}C of the six samples with different chemical compositions are calculated based on the quenched experiments. These rates are not only slightly site-specific, but also increase with Fe and tetrahedrally coordinated Al contents. Indeed, the Near-FTIR spectra suggest that the dehydration of the samples in this study involves oxidation of Fe^{2+}. For two diopsides with a mantle affinity, the diffusivity is about 10^{-12} m^2/s at 1000 °C. The results mainly have the following implications: (1) the different local environments of hydrogen defects between high *T* and low *T* may be responsible for the different mechanism of water impact on

electrical conductivity between high and low *T* experiments; (2) since the hydrogen diffusivities are positively related to Fe and ^{IV}Al contents, more care is required for interpretation of measured water concentrations for clinopyroxene samples with high Fe and ^{IV}Al contents. Compared between hydrogen diffusivities of olivine, orthopyroxene and clinopyroxene in mantle peridotite, clinopyroxene should be the most reliable recorder of water from depth.

Keywords: hydrogen defect, clinopyroxene, high temperature, diffusivity, *in situ* FTIR, electrical conductivity, effect mechanism

INTRODUCTION

The main minerals in the deep earth are nominally anhydrous minerals (NAMs), nevertheless, water can be incorporated as hydrogen defects which may strongly influence physical properties of NAMs, such as electrical conductivity, rheology and heat transferring (e.g., Mackwell et al. 1985; Karato 1990; Wang et al. 2006; Yoshino et al. 2008; Thomas et al. 2012; Faul et al. 2016; Chang et al. 2017), thereby affecting physical/chemical processes in the deep Earth (Peslier et al. 2010; Xia et al. 2013; Demouchy and Bolfan-Casanova 2016; Liu et al. 2017). However, the importance of water effect on several properties are still under current debates (e.g., Wang et al. 2006; Yoshino et al. 2006, 2008; Costa and Chakraborty 2008; Demouchy et al. 2012; Jones et al. 2012; Fei et al. 2013; Karato and Wang 2013; Yoshino and Katsura 2013; Dai and Karato 2015; Gardés et al. 2015). This is not only caused by differences in experimental methods, but also due to the complications in speciation of hydrogen defects (Karato 2015; Jones 2016). For instance, some recent experimental studies have reported that different hydrogen defects in NAMs have different effects on properties such as rheology and elasticity (e.g., Faul et al. 2016; Purevjav et al. 2016; Padrón-Navarta and Hermann 2017; Tielke et al. 2017). As a result, understanding speciation of hydrogen defects is fundamental to understand water effects on properties of NAMs. Theoretically, Karato (2006) speculated that speciation and sites of hydrogen defects in NAMs at high temperature may not be the same as those at room temperature. In fact, several studies have indicated that speciation of hydrogen defects at room temperature may be misleading for discussing physical mechanism of water effects on properties of NAMs at high temperature. For example, Aines and Rossman (1985) reported that water speciation in feldspar at high temperature was different from that at room temperature. Yang and Keppler (2011) reported that hydrogen defects assigned to Si vacancies in olivine were unstable with increasing temperature. Yang et al. (2011) and Guo (2017) have reported that water speciation in rutile at room temperature is not representative of that at high temperatures relevant for subduction zones or upper mantle conditions. Yang et al. (2015) and Liu et al. (2018) found unquenchable transferring of hydrogen defects between sites in anorthoclase with increasing temperature. Very recently, Qin et al. (2018) has shown by numerical modeling that water speciation in olivine could be influenced by temperature and pressure. Consequently, knowledge of hydrogen defects in NAMs at high temperatures is essential to understand if water effects on mantle physical properties are significant at temperature and pressure conditions of Earth mantle.

In addition, different hydrogen defects have different diffusivities at high temperature. Recent experimental studies have reported site-specific hydrogen diffusivities for Ti-doped Fe-free olivine and clinopyroxene, respectively (Padrón-Navarta et al. 2014; Ferriss et al. 2016). Those works provide bases for distinguishing multiple processes in the history of an olivine grain (Tollan et al. 2015) and permit evaluating if water observed in upper mantle minerals is representative of the deep mantle (Denis et al. 2018). However, the recent study on naturally hydrated olivine did not report drastic difference in diffusivities for various hydrogen defects (Thoraval et al. 2018). Thus, the lack of consensus is a call for further study on site-specific hydrogen diffusion, especially in clinopyroxene.

Indeed, clinopyroxene is one of the main constituent minerals in the lower crust and upper mantle. Clinopyroxene is the pyroxene with large cations such as Ca^{2+}, Na^{+} and Li^{+} occupied in the M2 sites in the structure, thereby with space group C2/c at ambient conditions. For example, the diopside-hedenbergite solid solution, augite, jadeite, omphacite, spodumene and aegirine are clinopyroxene minerals. Among them, the diopside and augite are calcic clinopyroxenes, jadeite, omphacite and aegirine are sodic clinopyroxenes, while spodumene is lithium aluminum silicate. Diopside is the main phase of the upper mantle peridotite. Hydrogen tends to partition into it rather than olivine and orthopyroxene (e.g., Aubaud et al. 2004; Grant et al. 2007; Demouchy et al. 2016). For diopside form mantle peridotite, water content ranges from 0 to 1000 wt. ppm (Demouchy et al. 2016). In addition, omphacite from mantle eclogite can contain water content up to 1800 ppm (Smyth et al. 1991). Yang et al. (2010, 2015) investigated the behavior of hydrogen defects in clinopyroxenes at temperatures between 20 and 500 °C. They found that the speciation and sites of hydrogen defects did not change over the temperature range, but the O-H bond stretching frequencies varied with different extent for different hydrogen defects. To date, defects in clinopyroxene under temperatures corresponding to the upper mantle remains unclear.

Consequently, in order to understand whether hydrogen defects observed at ambient conditions reflect their behavior at mantle temperatures, we investigated behavior of different hydrogen defects in clinopyroxenes at temperatures up to 1000 °C. Since nature of hydrogen defects is closely related to chemical environment, we chose ten clinopyroxene samples with different compositions (calcic and sodic clinopyroxenes, Fe-poor and Fe-rich clinopyroxenes) from various localities. We measured *in situ* Fourier transform infrared (FTIR) spectra of ten clinopyroxenes to monitor variations of hydrogen sites with increasing temperature. We also carried out quenched experiment at 1000 °C to determine hydrogen diffusivity of different OH groups. The Near-FTIR spectra of Fe^{2+} in the samples before and after dehydration were collected to qualify the dehydration mechanism. Those results provide information about what happens to hydrogen defects at atomic level during high temperature process, and contribute to further understanding preservation of hydrogen defects and their effect mechanisms on electrical conductivity at high temperatures.

MATERIALS AND METHODS

Sample description

Ten natural clinopyroxene single crystals from different localities were analyzed in this study: two gem-quality diopsides from Austria (diopside-Austria, with about 17 wt. ppm water) and Russia (diopside-Russia) which are previously described in Ingrin et al. (1989) and Andrut et al. (2007); a diopside in a marble xenolith from the Mount Marcy anorthosite massif at the Cascade Slide, New York, USA (diopside-marble), with 138 wt. ppm water reported in Johnson et al. (2002); two diopside crystals from Aksu, China (diopside-Aksu1, diopside-Aksu2), with 44 wt. ppm water reported in Shuai and Yang (2017); a diopside in peridotite xenolith hosted by Cenozoic basalt from Jiande, Zhejiang, China (diopside-JD), with 573 wt. ppm water reported in Hao et al. (2014); a diopside in peridotite xenolith (Mid-Atlantic Ridge) (diopside-deep sea, with 529 wt. ppm water, unpublished data); two augite megacrysts hosted by Cenozoic basalt from Yingfengling (augite-YFL) and Nushan (augite-NS), China, with less than 1 wt. ppm water reported by Yang and McCammon (2012); an omphacite from eclogites from the Roberts Victor kimberlite pipe, South Africa (omphacite), with 639 wt. ppm water reported by Huang et al. (2014). The samples are all C2/c clinopyroxenes (see the crystal structure data in the in the supplementary material). All samples were un-oriented and double polished single crystals. The samples with grain thickness ranging from 0.124 to 0.995 mm were used for the *in situ* high temperature FTIR spectra measurements. The samples with grain thickness ranging from 0.146 to 0.980 mm were used for the dehydration experiments.

Electron probe micro analyzer (EPMA)

The chemical compositions of the samples were determined using an EPMA 1600 (Shimadzu) electron microprobe at Zhejiang University (China). The analyses were performed with a 15 kV accelerating voltage, 10 nA beam current and a 5 μm beam diameter. Natural minerals were used as standards, and a program based on the ZAF procedure was applied for data correction. Multi-point measurements were conducted from core to rim of each mineral grain. The analyses demonstrate the chemical homogeneity of the samples. Reproducibility of multi-point analysis is <1% for elements with concentration >5% and <3% for elements with concentration >1%.

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Based on the average chemical compositions, the calculated cations per 6 oxygen atoms are listed in Table 1.

In situ Mid-FTIR spectroscopy

Unpolarized and polarized FTIR spectra in the frequency range 4000-1000 cm^{-1} were collected using a Nicolet iS50 FTIR spectrometer coupled with a Continuμm microscope at Zhejiang University (China). A KBr beam-splitter and a liquid nitrogen-cooled MCT-A detector were used. A total of 128 scans were accumulated for each spectrum at a 4 cm^{-1} resolution. The squared aperture size was set to 50×50 μm. Background was collected at every temperature. Spectra were collected on the same selected area for each sample.

For the *in situ* high temperature measurements, the samples were placed on a Pt foil with a hole of 1.5 mm in diameter or on a sapphire plate in a heating stage with CaF_2 windows, equipped with a resistance heater and an S-type thermocouple. The sample was heated in N_2. The sample temperature was determined with an uncertainty of less than 1 °C. The temperature was increased from 20 to 1000 °C using a heating rate of 15 ˚C/min. For every temperature step, except otherwise indicated, the dwell time was 5 minutes.

Quenched dehydration experiments

We choose six clinopyroxene samples with different chemical composition for dehydration experiments. The experimental conditions and sample thickness are listed in Table 2. They were annealed in the heating stage at a desired temperature of 1000 ˚C for different hours, respectively. To avoid oxidation by the air, the heating stage was purged with N_2 of high purity during the annealing. Then FTIR measurements were carried out on the samples after quenching to room temperature.

Near-FTIR (NIR) spectroscopy

To investigate variations of Fe^{2+} in the samples before and after dehydration, NIR spectra in the frequency range 12000-4000 cm^{-1} were collected using a Bruker

Vertex70 FTIR spectrometer coupled with a hyperion1000 microscope at Zhejiang University (China). A CaF_2 beam-splitter and an InGaAs detector were used. A total of 64 scans were accumulated for each spectrum at a 4 cm^{-1} resolution. The squared aperture size was set to 50×50 μm. Spectra were collected on the same selected area for each sample.

Data analysis

For *in situ* experiment, to analyze site-specific temperature dependence of each OH band in the samples, spectra were decomposed using the Peakfit v4.12 software. Width, amplitude and frequency of every single band were adjustable to obtain the best peakfitting. For several samples with broad and significantly overlapped bands, we used OMNIC7.1 software to obtain the bulk integral absorbances, because peakfitting may not be the best way to extract absorbances (Zhang et al. 2007).

For the quenched experiment, we applied OMNIC7.1 software to obtain the bulk integral absorbance and calculate the bulk hydrogen diffusivity. Peakfit was used to obtain the integral absorbance of each OH band and calculate the site-specific hydrogen diffusivity. Based on dimensions of the samples, hydrogen diffusivities of the bulk hydrogen defects and site-specific hydrogen defect were obtained using the one-dimensional model of diffusion from Ingrin et al. (1995). In the calculation of OH concentration ratio of the final to initial concentration as a function of heating time, we used the ratio of the final to initial peak area, rather than the absolute water concentration. The resulting dehydration data were listed in Table 2.

RESULTS

Hydrogen defects at ambient conditions

As commonly observed in natural clinopyroxene (e.g., Skogby et al. 1990), four groups of OH absorption bands are found in the ten samples: 3620-3640 cm^{-1} (group 1), 3530-3540 cm^{-1} (group 2), 3460 cm^{-1} (group 3) and 3360 cm^{-1} cm^{-1} (group 4) as shown in Figure 1. Not every OH band is prominent in all samples because of the differences in thickness, chemical composition and crystallographic orientation of the samples. Among the ten samples, the FTIR spectra of the diopside-Austria and diopside-Russian, the diopside-marble, the diopside-Aksu have also been reported in Ingrin et al. (1989), Johnson et al. (2002), Shuai and Yang (2017), respectively. It should be noted that the band of group 1 at 3620-3640 cm^{-1} in omphacite may not be intrinsic but related to nanometer-sized inclusions within the crystals (Koch-Müller et al. 2004), thus we did not consider further this OH band of omphacite in the rest of the study.

Cation substitutions usually cause shifts in band positions (Libowitzky and Beran 2006). Combined with the previously reported and some unpublished data of clinopyroxene, positions of the OH bands of group 1 are plotted versus chemical compositions in Figure 2. The band position correlates roughly with the amount of tetrahedral coordinated Al^{3+} (^{IV}Al) (Fig. 2a, b). This supports the assignment of the group 1 band to coupled substitution of Al^{3+} and H^{+} in Si vacancy (e.g., Skogby et al. 1990; Bromiley and Keppler 2004; Gavrilenko et al. 2010). To date, the band of group 2 lacks a clear compositional association. Some studies suggested that it was related to substitution of H in M2 site or coupled substitution of H with some lower valence cations in M1 site (Skogby et al. 1990; Bromiley and Keppler 2004), while Koch-Müller et al. (2004) assigned it again to coupled substitution of Al^{3+} and H^{+} for Si vacancy. Based on the relationship between OH frequencies and chemical compositions, we further divide the group 2 OH band into the group 2a with OH wavenumbers higher than 3535 cm^{-1} and the group 2b with OH wavenumbers lower than 3535 cm^{-1} (Fig. 2b, c). The group 2a OH is related to tetrahedral coordinated Al^{3+}, which is consistent with the assignment in Koch-Müller et al. (2004). In agreement with Skogby et al. (1990) and Bromiley and Keppler (2004), the group 2b OH could be related to vacant M sites. Figure 2 also indicates that group 3 band may be related to the vacant M site, consistent with the assignment of it to coupled substitution of H and trivalent cation in M2 (Smyth et al. 1991; Koch-Müller et al. 2004; Stalder and Ludwig 2007). The group 4 is rare in natural samples and only exists in the diopside-Austria and diopside-Aksu2 in this study. These two diopsides have much more M vacancies when compared to the others. It may be related to a higher M vacancy concentration than in other samples, thus supporting the assignment of H substitution in Mg vacancies (Stalder and Ludwig 2007). The negative vacancy may be due to the presence of ferric iron (Fe^{3+}) in these samples, which we neglected in the calculations. Indeed, the sample with the most negative vacancy is the Fe^{3+}-rich augite. Yang and McCammon (2012) reported that the augite-NS contains 34% of the total Fe as Fe^{3+}.

Behavior of hydrogen defects at high temperatures

OH bands at elevated temperatures

Figure 3 shows the unpolarized FTIR spectra of the clinopyroxenes at different temperatures (see the polarized FTIR spectra in the supplementary material). With increasing temperature, most bands gradually weaken, broaden and even diminish, especially for the bands at lower frequencies. A new OH band around 3443 cm^{-1} also appears in the spectra of the diopside-Austria and diopside-Aksu2 quenched from 1000 °C.

In Figure 4, site-specific band shifts with increasing temperature are reported. With increasing temperature, the band of group 1 linearly shifts to lower wavenumbers but to different extents for the studied samples, while the band of group 4 linearly shifts to higher wavenumbers. For most samples, the group 2 and group 3 bands significantly overlapped and disappeared at high temperatures, thus, we only display the data of samples with the prominent group 2 and group 3 bands. With increasing temperature, the group 2 and group 3 bands generally shift to lower wavenumbers, but not linearly or as drastically as the group 1 band does. The group 3 band of the diopside-Austria and diopside-Aksu2 shifts to higher wavenumbers with increasing temperature to 800 °C, then shift to lower wavenumbers.

Furthermore, there is a decrease in the absorption of the OH bands at elevated temperatures, especially for the augite-YFL and omphacite with almost no absorption at 1000 and 700 °C, respectively. Comparing between the FTIR spectra of the ten samples before heated and after quenched from 1000 °C, it is clear that dehydration has occurred during the heating process for most of the samples. In order to explore at which temperature dehydration starts, we analyzed variations of the OH absorbances. The evolution of the bulk integral absorbance of the OH bands with temperature is shown in Figure 5. With increasing temperature, the bulk integral absorbance exhibits little variation for the diopside-marble, while it displays a turning point with drastic decrease at the temperature above 600 °C for the diopside-Austria, diopside-Aksu1, diopside-JD, diopside-Russia, augite-YFL and augite-NS. In contrast, the turning point appears earlier at 300 °C in the evolution of the bulk integral absorbance of OH bands in the diopside-Aksu2 with temperature. Unfortunately, for most samples, the OH bands significantly overlap at high temperatures. This impedes the accurate analysis of absorbance of each OH band (Zhang et al. 2007). We choose the diopside-Austria and diopside-Aksu2 with well separated OH bands and show their site-specific evolution in Figure 5. The absorbances of the bands of group 1, group 3 and group 4 in the diopside-Austria keep steady, then drastically decrease at 700 ^{o}C. For the diopsde-Aksu 2, the absorbances of the bands of group 3 and group 4 do not change until increasing temperature to 500 and 700 ^{o}C, respectively, while the absorbance of the group 2b band decrease first then increase with increasing temperature to 700 ^{o}C.

Hydrogen diffusivities at 1000^{o}C

To investigate dehydration at high temperature, we conducted dehydration experiments at 1000 ^{o}C on six samples with different chemical compositions. The evolutions of the FTIR spectra with annealing time are shown in Figure 6. The bulk and site-specific diffusion coefficients were obtained by fitting the data using a one-dimensional model of diffusion as in Ingrin et al. (1995) and reported in Table 2. The hydrogen diffusion coefficient is different not only between samples, but also between hydrogen defects in the same sample. For example, the bulk hydrogen diffusivities are the slowest in the diopside-marble and diopside-Russia ($6\text{-}7\times10^{-13}$ m^2/s), moderate in the diopsides from mantle peridotite (diopside-deep sea and

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diopside-JD) (1×10^{-12} m^2/s), and the fastest in the diopside-Austria and augite-NS (6×10^{-12} m^2/s). Moreover, it seems that the site-specific hydrogen diffusivity is following different order between samples. For the diopside-marble, the diopside-Russia and the augite-NS, the diffusivity of hydrogen responsible for the OH band in group 1 is lower than that of the group 2. However, it is a little faster than that of the group 2 for the diopside-deep sea and diopside-JD. We have reported the bulk and site-specific diffusion coefficients as a function of chemical composition of the six samples in Figure 7. There are satisfying positive correlations between hydrogen diffusivities and chemical compositions except for the diopside-Austria. The presence of microscopic amphibole lamellae previously reported by Ingrin et al. (1989) in this sample could be a reason for its abnormal behavior. The lamellae provide possible shortcuts for diffusion. Excluding the diopside-Austria, the bulk and site-specific hydrogen diffusivities increase with the Fe and ^{IV}Al contents. The diffusivity of the group 1 OH is more correlated with ^{IV}Al content, while that of the group 2 OH is more correlated with Fe content. The bulk hydrogen diffusivity is more correlated with Fe than ^{IV}Al content. In contrast to the temperature dependence of O-H bond strength, we did not find any clear relationship between hydrogen diffusivity and its corresponding band frequency. Thus, the difference of chemical composition has much more effect on hydrogen diffusivity than the peak-specific difference does.

Variation of Fe^{2+} in the samples before and after dehydration

To explore the dehydration mechanism, Figure 8 compares the NIR spectra of the clinopyroxene samples before and after the dehydration experiments. The bands around 10,500 and 9500 cm^{-1} are assigned to crystal field bands (CFB) due to d-d transitions of Fe^{2+} at M1 and M2 sites, respectively (Rossi et al. 1987; Burns et al. 1993). After dehydration, the absorbances of Fe^{2+} at both M1 and M2 sites decrease for the diopside-Austria and diopside-Russia, while only the absorbances of Fe^{2+} at M2 sites decrease for the two diopsides from mantle peridotite and the augite-NS.

DISCUSSION

Variations of local environments of hydrogen defects with increasing temperature

The frequency of an OH band reflects the strength of O-H bond. The site-specific frequency shift of OH bands in clinopyroxene with increasing temperature indicates different local environments of the hydrogen defects within their structures. The negative frequency shifts of the group 1 OH bands indicate temperature-induced lengthening and weakening of O-H bonds. The positive frequency shifts of the group 4 OH bands suggest weakening of hydrogen bonds (H…O) with increasing temperature, because weakening of hydrogen bonds will induce a relative strengthening of the primary O-H bond (Nakamoto et al. 1955; Xu et al. 2013). The moderate negative frequency shifts of the groups 2 and 3 OH bands may indicate the simultaneous action of the lengthening of O-H and H…O bonds. One can speculate on a possible correlation between the initial frequency and its temperature dependence. We show the temperature dependence of OH frequency as a function of initial frequency for the clinopyroxene samples in this study and also for several minerals from previous studies for comparison in Figure 9a. A near linear relation exists between the temperature dependence of OH frequencies and their frequency at room temperature for silicate minerals. The room-temperature frequency corresponding to the cut-off between the positive and negative shift is around 3400 cm^{-1}. The low-temperature evolution of OH bands in forsterite also suggests this rough relationship (Ingrin et al. 2013). However, as shown in Figure 9a, the results for rutile do not lie along the trends probably due to the very different structures of silicate and oxide minerals.

In contrast to the resolved OH bands at room temperature, the IR spectra at 1000 ^oC display only one broad band. The one broad band at high temperature can arise from a statistical distribution across multiple sites or hydrogen disordering in the clinopyroxene structure. Based on the relationship between OH frequency and O-O distance (Libowitzky 1999), we can provide some constraints on the hydrogen bonding environments of hydrogen defects at room temperature and at 1000 ^oC

(Figure 9b). For the group 1 OH with frequencies around 3571-3553 cm^{-1} at 1000 ^oC, the predicted O-O distance is about 3.0 Å. For the group 2 OH with frequencies around 3510-3469 cm^{-1} at 1000 ^oC, respectively, the predicted O-O distance is about 2.9 Å. For the group 3 OH with frequencies around 3476-3417 cm^{-1} at 1000 ^oC, the predicted O-O distance is about 2.9-2.8 Å. For the group 4 OH with frequencies around 3398-3387 cm^{-1} at 700 ^oC, the predicted O-O distance is about 2.8 Å. Obviously, the O-O distances for the four groups OH at 1000 ^oC are more centralized than those observed at room temperature (Fig. 9c). Thus, the one broad band at high temperature such as 1000 ^oC is interpreted here as temperature-induced hydrogen disordering across multiple bonding sites with similar O-O distances. Temperature or pressure-induced hydrogen disordering was also expected in the structures of wadsleyite and ringwoodite (Kohn et al. 2002; Panero et al. 2013).

Site-specific thermal stability of the hydrogen defects

According to the Beer-Lambert relationship, $A = \varepsilon ct$, absorbance of O-H vibration relates to absorption coefficient of O-H, water concentration and sample thickness (ε is the absorption coefficient, A the measured integrated absorbance, t the sample thickness, and c the concentration of the molecule studied). Previous studies have shown that dehydration in diopside and augite could be neglected during the short heating process from room temperature to 500 °C (Yang et al. 2010, 2015). Additionally, contribution of the variation in sample thickness can be neglected below 500°C based on the thermal expansion of clinopyroxene (Pandolfo et al. 2015). Furthermore, *in situ* polarized FTIR spectra (see supplementary material) at elevated temperature indicate that O-H orientation does not significantly change with temperature. Thus, the slight variation before the turning point in the evolution of the integral absorbance with temperature indicates temperature dependence of OH absorption coefficient. According to Barron (1962), the absorption coefficient of a fundamental vibration transition is proportional to the square of the change of dipole moments. Extensive studies have suggested that absorbance coefficient of O-H in glasses and hydrous minerals is temperature dependent (e.g., Keppler and

Bagdassarov 1993; Withers et al. 1999; Zhang et al. 2007, 2016; Tokiwai and Nakashima 2010; Della Ventura et al. 2017). However, only few studies addressed temperature dependence of absorption coefficient of O-H vibration of hydrogen defects in NAMs (Yang et al. 2010, 2012, 2015).

In contrast to the slight variations at low temperatures, the dramatic decrease of the integral absorbance above the turning point at higher temperatures is due to dehydration. For most samples in this study, dehydration begins at temperatures above 600 °C. However, the diopside-Aksu2 starts dehydrating as early as 300 °C, while hydrogen defects in the diopside-marble are the most stable with negligible dehydration during the heating process. The dominant OH band belongs to the group 1 in the diopside-marble, while they belong to the groups 2, 3 and 4 in the diopside-Aksu2. It seems that the bands of group 1 are more stable than the ones of the other groups. Thus, it is expected that different hydrogen defects have distinct thermal stability. Indeed, in the diopside-Aksu2, dehydration of the group 3 starts at 500 °C, while the group 2b starts dehydrating at 200 °C and then re-hydrates at 700 °C. Dehydration of the group 4 starts at 700°C, which may account for the re-hydration of the group 2b. However, the group 1, group 3 and group 4 in the diopside-Austria start dehydrating at the same temperature. It is generally accepted that breaking of O-H bonds must occur during the dehydration. Therefore, we attempt to explain the different thermal stabilities of the hydrogen defects using the temperature dependence of O-H bond strength. Note that the O-H bond corresponding to the group 1 OH bands weakens, while that related to the group 4 OH bands strengthens with increasing temperature. Thus, it will be taken for granted that the hydrogen defects of the group 1 are most unstable defects, which was never demonstrated before. Consequently, the driving force for the dehydration remains complex.

Dehydration mechanism and origin of the band at 3443 cm^{-1}

Similar to Ferriss et al. (2016), we found that different hydrogen defects have different diffusivities. Ferriss et al. (2016) proposed that the hydrogen defects of the

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group 2 OH band diffuse faster than those of the group 1 OH band based on their two diopside samples. Based on the data in this study, we do not find a uniform behavior of the diffusivities for different OH bands. In the diopside-marble, diopside-Russia and augite-NS, the hydrogen defects of the group 2 OH diffuse faster than those of the group 1, in agreement with Ferriss et al. (2016). However, in the two diopsides from mantle peridotite, the hydrogen defects of the group 2 OH band diffuse slightly slower than those of the group 1 OH band. But the difference between OH bands in clinopyroxene is not by more than one order of magnitude, far less than in Ti-doped Fe-free forsterite (Padrón-Navarta et al. 2014). In contrast, hydrogen diffusivities are mainly controlled by chemical compositions of the samples. Consistent with previous studies (Skogby and Rossman 1989; Ferriss et al. 2016), the bulk hydrogen diffusivities increase with Fe content (a.p.f.u.). For the two diopsides from mantle peridotites with Fe around 0.07-0.08 a.p.f.u., the bulk diffusivity is on the order of 10^{-12} at 1000 ^{o}C, one order of magnitude slower than the prediction of Ferriss et al. (2016). Contrary to Ferriss et al. (2016), we obtain a positive relationship between the bulk hydrogen diffusivities and ^{IV}Al content based on our data. We can further find relationships between site-specific hydrogen diffusivities and chemical compositions. For example, the diffusivity of hydrogen defects related to the group 1 OH band is more dependent on ^{IV}Al content, while that of the group 2 OH band is more dependent on Fe content. Thus, for the augite samples with high Fe and high ^{IV}Al, hydrogen defects diffuse very fast.

As for hydrogen diffusion mechanism, there are self-diffusion deduced from H-D exchange experiment, chemical diffusion controlled by the mobility of polarons and chemical diffusion controlled by the mobility of metal vacancies (Ingrin and Blanchard 2006). Among them, the mobility of polarons involves the oxidation-reduction of iron. In this study, the absorbances of Fe^{2+} decrease with dehydration. Thus, the dehydration mechanisms of the clinopyroxene samples involve oxidation of Fe^{2+}: $Fe^{2+} + OH^- = Fe^{3+} + O^{2-} + 1/2H_2$. That is just what we observed in relationship between hydrogen diffusivity and Fe content. Strictly speaking, the view that extraction of H is a linear function of iron is an oversimplification. In fact, what is important is the number of Fe^{2+} available for the reaction. Based on the initial absorbances of Fe^{2+} in these samples, the content of Fe^{2+} is positively related to the bulk Fe content. Therefore, using bulk Fe content in this study does not significantly change the main results.

The band at 3443 cm^{-1} is not common in natural diopsides, but it has been previously observed in synthetic Fe- and Na-doped diopsides (Stalder and Ludwig 2007; Purwin et al. 2009). Based on the similar pleochroic behavior of the bands at 3360 and 3443 cm^{-1}, Purwin et al. (2009) assigned the band at 3443 cm^{-1} to a coupled substitution of a ferric iron and a proton to two neighboring Mg vacancies. Skogby and Rossman (1989) reported the new band around 3443 cm^{-1} appearing in the FTIR spectra of diopside from India after heating in H_2 or air and ascribed it to the lower frequency shift of the 3460 cm^{-1} band. Ferriss et al. (2016) also observed the increase of the band around 3443 cm^{-1} in the FTIR spectra of Kunlun diopside and Jaipur diopside after gently heating. They suggested that this additional hydrogen was taken up from the surroundings in the furnace, or was originally present in hydrous microinclusions, or initially distributed evenly among the various initial peaks. Thus, the origin of this new band has not been elucidated. In this study, the new band at 3443 cm^{-1} only occurs in the FTIR spectra of the diopside-Austria and Aksu2 quenched from high temperatures. Moreover, the 3443 cm^{-1} band seems to have an orientation similar to the band at 3460 cm^{-1} related to the group 3 (Figure 10b). Therefore, the band at 3443 cm^{-1} could be assigned to a new hydrogen defect in M site. To draw some relationships between this new hydrogen defect and hydrogen defects corresponding to other OH bands, variations of integral absorbances of the deconvoluted bands of the quenched sample with isothermal annealing time are plotted in Figure 10. With annealing time, the integral absorbance of the 3443 cm^{-1} band slightly increases, the integral absorbance of the 3467 cm^{-1} band shows little variation, while those of the 3645 and 3359 cm^{-1} bands decrease. As a result, it is unlikely that the hydrogen defect corresponding to the new band is related to hydrogen defect corresponding to the 3467 cm^{-1} band. Since hydrogen defect corresponding to the 3645 cm^{-1} band is located in Si site, it is most likely that the 3443 cm^{-1} band is related to hydrogen defect corresponding to 3359 cm^{-1} which is located in M site. In contrast to other samples, only these two samples have the group 4 OH band at 3359 cm^{-1}, which also supports our conclusion. Since dehydration mechanism of the diopside from Austria involved the oxidation of Fe^{2+} to Fe^{3+}, the 3443 cm^{-1} band could be a new hydrogen defect in M site, coupled with the ferric iron formed during dehydration, in agreement with Purwin et al. (2009).

IMPLICATIONS

Hydrogen speciation and sites in the clinopyroxene at high temperatures: effect mechanism on electrical conductivity

It is well established that hydrogen defects can influence electrical conductivity of their host minerals. However, there are discrepancies among published experimental results (e.g., Wang et al. 2006; Yoshino et al. 2006, 2008; Karato and Wang 2013; Yoshino and Katsura 2013). In view of these long standing discrepancies, Karato (2013, 2015) proposed a new theoretical model and suggested that the rate-controlling diffusing species of hydrogen-assisted electrical conductivity are different from those of H-D isotopic exchange. This model provides a good explanation of some discrepancies among the different experimental observations at different temperatures. Moreover, Dai and Karato (2014) showed by experiment that the mechanism of electrical conductivity of olivine changed with temperature, which is also observed for mantle clinopyroxene by Zhao and Yoshino (2016). Based on the model of Karato (2013), they proposed that the diffusion of protons in M site is the dominant contribution to electrical conductivity at high temperatures, while free protons at low temperatures. Although these results are well explained by the model (Karato 2013), there has been no direct observation of the changes of free protons at low temperatures to two protons in M site at high temperatures.

FTIR spectra are good tracers for local environments of hydrogen defects. From the *in situ* FTIR spectra at elevated temperatures in this study, we do not find a coupled growth and decline of OH bands as in rutile, anorthoclase or talc (Zhang et al. 2006; Yang et al. 2011, 2015; Guo 2017). This suggests that protons do not transfer easily between sites in the clinopyroxenes with increasing temperature up to 1000 ^{o}C. However, the local environments of hydrogen defects change with increasing temperature. At high temperatures, the four groups of hydrogen defects have similar O-O distances and display disordering in the structure. In contrast, the four groups of hydrogen defects have distinct O-O distances and show ordering in the structure at room *T*. Thus, it is unlikely that the water-effect on physical properties at high *T* is the same as that as low *T*. At high *T*, the strength of bonding between protons and the surrounding atoms are similar among the four groups of hydrogen defects. The protons belonging to the four groups of hydrogen defects likely have similar mobility at high *T*; this is likely not the case at low *T*. Therefore, the different local environments of hydrogen defects between high *T* and low *T* can be responsible for the different activation enthalpy of electrical conductivity between high and low *T* experiments observed by Dai and Karato (2014) and Zhao and Yoshino (2016). In addition, the pleochroism of hydrogen defects at high temperatures is not as prominent as at room temperature (see supplementary material). Thus, it can be inferred that anisotropy in electrical conductivity of clinopyroxene is also different between high and room temperature, which deserves to be tested in the future work.

This study extends the understanding of hydrogen speciation and sites in clinopyroxene at temperatures relevant to the lower crust and upper mantle. As conditions relevant of the deep Earth involve both high pressure and high *T*, the local environments of hydrogen defects in clinopyroxene at geologic conditions is simultaneously constrained by high pressure and high temperature. To date, no data have been reported for the high pressure behavior of hydrogen defects in clinopyroxene. Previous *in situ* high pressure spectroscopic investigations on olivine, wadsleyite and ringwoodite indicated that effect of pressure on variation in O-H bond strength is the contrary to the temperature effect (Cynn and Hofmeister 1994;

Jacobsen et al. 2005; Chamorro Pérez et al. 2006; Koch-Müller et al. 2011; Panero et al. 2013; Yang et al. 2014; Sakurai et al. 2015). Thus, it may be inferred the local environments of hydrogen defects in clinopyroxene at high temperature and high pressure is the same as ambient conditions. To fully address behavior of hydrogen defects in clinopyroxene under deep earth conditions, simultaneous *in situ* high temperature and high pressure FTIR spectroscopic investigations have to be carried out.

Preservation of hydrogen speciation and content in quenched clinopyroxene

Our *in situ* heating experiments indicate that hydrogen speciation in clinopyroxene does not change at least before dehydration. However, the dehydration experiments by quenching induced slight modifications of hydrogen speciation. In this case, a new band appears at 3443 cm^{-1}, which is linked to the dehydration process involving the oxidation of iron. Therefore, the occurrence of this band if observed in some natural clinopyroxenes could be used as a marker of a previous dehydration in oxidizing conditions.

The hydrogen diffusivities are positively related to Fe and ^{IV}Al contents in the clinopyroxene samples. Thus, for clinopyroxene samples with high Fe and ^{IV}Al contents, more care is required for interpretation of measured water concentrations. Based on the existing diffusivities of hydrogen in olivine and pyroxene, Denis et al. (2018) concluded that the remaining hydrogen concentrations observed in peridotites might only represent the “tip of the iceberg” of the water stored in the Earth's upper mantle. However, the hydrogen diffusivity in mantle-derived clinopyroxene was not available yet for referring in Denis et al. (2018). We provide here for the first time the hydrogen diffusivity at 1000 ^oC in the mantle-derived diopside, and we show that its diffusion coefficient may be one order of magnitude lower than that used in Denis et al. (2018). For the hydrogen diffusivity controlled by the proton-vacancy mechanism, it is similar and range between the diffusivities of olivine, enstatite and diopside, e.g., 6×10^{-12}, 1.3×10^{-11}, and 3.1×10^{-11} m^2/s at 1100^oC, respectively (Demouchy and Mackwell 2006; Carpenter Woods 2001; Ferriss et al. 2016). The similar diffusivities cannot explain the mineral specific hydrogen concentrations in the mantle xenoliths. Therefore, the hydrogen diffusivity controlled by the proton-polaron mechanism may in fact contribute to a different preservation of hydrogen in the olivine, enstatite and diopside. In this study, the hydrogen diffusivity in the diopside samples is controlled by the proton-polaron mechanism. It ranges between 1×10^{-12} and 1.2×10^{-12} m^2/s at 1000 ^oC in the two diopsides from mantle peridotites, two orders of magnitude lower than 4×10^{-10} m^2/s in mantle olivine (Mackwell and Kohlstedt 1990), and slightly lower than 4×10^{-12} m^2/s in mantle enstatite (Carpenter Woods 2001) at the same temperature. It should be noted that the dehydration experiment in this study is carried out in open system and ambient pressure, thus, the hydrogen diffusivity may be lower than 10^{-12} m^2/s at 1000 ^oC in a closed system. As a result, clinopyroxene should be the most reliable recorder of water from depth compared with the mantle olivine and orthopyroxene, which was already inferred by Tian et al. (2016). Moreover, this study shows that the hydrogen diffusivity of the group 1 OH (3620-3640 cm^{-1}) increases with ^{IV}Al content, and that of the group 2 OH (3530-3540 cm^{-1}) increase with Fe content. For the two diopsides from mantle peridotites, the hydrogen diffusivity at 1000 ^oC of the group 1 OH (3640 cm^{-1}, with the hydrogen diffusivity of 1.6×10^{-12}) is slightly higher than that of the group 2 OH (3540 cm^{-1}, with the hydrogen diffusivity of 1.2×10^{-12}). This site-specific difference is quite low and much less than the difference caused by chemical composition. Therefore, preservation of water in mantle clinopyroxene mainly depends on chemical composition.

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REFERENCES

Aines, R.D., and Rossman, G.R. (1985) The high temperature behavior of trace hydrous components in silicate minerals. American Mineralogist, 70, 1169-1179.

Andrut, M., Wildner, M., Ingrin, J., and Beran, A. (2007) Mechanisms of OH defect incorporation in naturally occurring, hydrothermally formed diopside and jadeite. Physics and Chemistry of Minerals, 34, 543-549.

Aubaud, C., Hauri, E.H., and Hirschmann, M.M. (2004) Hydrogen partition coefficients between nominally anhydrous minerals and basaltic melts. Geophysical Research Letters, 31 (20).

Barrow, G.M. (1962) Introduction to molecular spectroscopy. Mc-Graw-Hill, New York, 76-80.

Bromiley, G.D., and Keppler, H. (2004) An experimental investigation of hydroxyl solubility in jadeite and Na-rich clinopyroxenes. Contributions to Mineralogy and Petrology, 147, 189-200.

Burns, R.G. (1993) Mineralogical applications of crystal field theory, 2nd edn. Cambridge University Press, Cambridge.

Carpenter Woods, S. (2001) The Kinetics of Hydrogen Diffusion in Single Crystal Orthopyroxene. (PhD thesis). Dept. Geosciences. Pennsylvania State University.

Chamorro Pérez, E.M., Daniel, I., Chervin, J.C., Dumas, P., Bass, J.D., and Inoue, T. (2006) Synchrotron IR study of hydrous ringwoodite (γ-Mg_2SiO_4) up to 30 GPa. Physics and Chemistry of Minerals, 33, 502-510.

Chang, Y.Y., Hsieh, W.P., Tan, E., and Chen, J.H. (2017) Hydration-reduced lattice thermal conductivity of olivine in Earth's upper mantle. Proceedings of the National Academy of Sciences of the United States of America, 114, 4078.

Costa, F., and Chakraborty, S. (2008) The effect of water in Si and O diffusion rates in olivine and implications for the transport properties and processes in the upper mantle. Physics of the Earth and Planetary Interiors, 166, 11-29.

Cynn, H., and Hofmeister, A.M. (1994) High-pressure IR spectra of lattice modes and

OH vibrations in Fe-bearing wadsleyite. Journal of Geophysical Research, 99, 17717-17727.

Dai, L., and Karato, S. (2014) High and highly anisotropic electrical conductivity of the asthenosphere due to hydrogen diffusion in olivine. Earth and Planetary Science Letters, 408, 79-86.

Dai, L., and Karato, S. (2015) Reply to comment on “High and highly anisotropic electrical conductivity of the asthenosphere due to hydrogen diffusion in olivine” by Dai and Karato [Earth Planet. Sci. Lett. 408 (2014) 79-86]. Earth and Planetary Science Letters, 427, 300-302.

Della Ventura, G., Susta, U., Bellatreccia, F., Marcelli, A., Redhammer, G.J., and Oberti, R. (2017) Deprotonation of Fe-dominant amphiboles: Single-crystal HT-FTIR spectroscopic studies of synthetic potassic-ferro-richterite. American Mineralogist, 102, 117-125.

Demouchy, S., and Mackwell, S. (2006) Mechanisms of hydrogen incorporation and diffusion in iron-bearing olivine. Physics and Chemistry of Minerals, 33, 347-355.

Demouchy, S., Tommasi, A., Barou, F., Mainprice, D., and Cordier, P. (2012) Deformation of olivine in torsion under hydrous conditions. Physics of the Earth and Planetary Interiors, 202-203, 75-70.

Demouchy, S., and Bolfan-Casanova, N. (2016) Distribution and transport of hydrogen in the lithospheric mantle: A review. Lithos, 240-243, 402-425.

Demouchy, S., Thoraval, C., Bolfan-Casanova, N., and Manthilake, G. (2016) Diffusivity of hydrogen in iron-bearing olivine at 3 GPa. Physics of the Earth and Planetary Interiors, 260, 1-13.

Denis, C.M.M., Demouchy, S., and Alard, O., (2018) Heterogeneous hydrogen distribution in orthopyroxene from veined mantle peridotite (San Carlos, Arizona): Impact of melt-rock interactions. Lithos, 302-303, 298-311.

Faul, U., Cline, C.J., David, E.C., Berry, A.J., and Jackson, I. (2016) Titanium-hydroxyl defect-controlled rheology of the Earth’s upper mantle. Earth and Planetary Science Letters, 452, 227-237.

Fei, H., Wiedenbeck, M., Yamazaki, D., and Katsura, T. (2013) Small effect of water on uppermantle rheology based on silicon self-diffusion coefficients. Nature, 213-215.

Ferriss, E., Plank, T., and Walker, D. (2016) Site-specific hydrogen diffusion rates during clinopyroxene dehydration. Contributions to Mineralogy and Petrology, 171, 1-24.

Gardés, E., Gaillard, F., and Tarits, P. (2015) Comment to “High and highly anisotropic electrical conductivity of the asthenosphere due to hydrogen diffusion in olivine” by Dai and Karato [Earth Planet. Sci. Lett. 408 (2014) 79-86]. Earth and Planetary Science Letters, 427, 296-299.

Gavrilenko, P., Ballaran, T.B., and Keppler, H. (2010) The effect of Al and water on the compressibility of diopside. American Mineralogist, 95, 608-616.

Grant, K., Ingrin, J., Lorand, J.P., and Dumas, P. (2007) Water partitioning between mantle minerals from peridotite xenoliths. Contributions to Mineralogy and Petrology, 154 (1), 15-34.

Guo, H. (2017) In-situ infrared spectra of OH in rutile up to 1000°C. Physics and Chemistry of Minerals, DOI 10.1007/s00269-017-0881-6.

Hao, Y.T., Xia, Q.K., Li, Q.W., Chen, H., and Feng, M. (2014) Partial melting control of water contents in the Cenozoic lithospheric mantle of the Cathaysia block of South China. Chemical Geology, 380, 7-19.

Hao, Y.T., Xia, Q.K., Jia, Z.B., Zhao, Q.C., Li, P., Feng, M., and Liu, S.C. (2016) Regional heterogeneity in the water content of the Cenozoic lithospheric mantle of Eastern China. Journal of Geophysical Research-solid Earth, 121, 517-537.

Huang, J.X., Li, P., Griffin, W.L., Xia, Q.K., Greau, Y., Pearson, N.J., and O’Reilly, S.Y. (2014) Water contents of Roberts Victor xenolithic eclogites: primary and metasomatic controls. Contributions to Mineralogy and Petrology, 168, 1092.

Ingrin, J., Latrous, K., Doukhan, J.C., and Doukhan, N. (1989) Water in diopside: An electron microscopy and infrared spectroscopy study. European Journal of Mineralogy, 1, 327-341.

Ingrin, J., Hercule, S., and Charton, T. (1995) Diffusion of hydrogen in diopside: Results of dehydration experiments. Journal of Geophysical Research, 100, 15489-15499.

Ingrin, J., and Blanchard, M. (2006) Diffusion of Hydrogen on Minerals. Review of Mineralogy & Geochemistry, 62, 291-320.

Ingrin, J., Liu, J., Depecker, C., Kohn, S.C., Balan, E., and Grant, K.J. (2013) Low-temperature evolution of OH bands in synthetic forsterite, implication for the nature of H-defects at high pressure. Physics and Chemistry of Minerals, 40, 499-510.

Jacobsen, S.D., Demouchy, S., Frost, D.J., Ballaran, T.B., and Kung, J. (2005) A systematic study of OH in hydrous wadsleyite from polarized FTIR spectroscopy and single-crystal X-ray diffraction: Oxygen sites for hydrogen storage in Earth's interior. American Mineralogist, 90, 61-70.

Johnson, E.J., Rossman, G.R., Dyar, M.D., and Valley, J.W. (2002) Correlation between OH concentration and oxygen isotope diffusion rate in diopsides from the Adirondack mountains New York. American Mineralogist, 87, 899-908.

Jones, A.G., Fullea, J., Evans, R.L., and Muller, M.R. (2012) Water in cratonic lithosphere: calibrating laboratory-determined models of electrical conductivity of mantle minerals using geophysical and petrological observations. Geochemistry Geophysics Geosystems, 13, 360-366.

Jones, A. (2016) Proton conduction and hydrogen diffusion in olivine: an attempt to reconcile laboratory and field observations and implications for the role of grain boundary diffusion in enhancing conductivity. Physics and Chemistry of Minerals, 43, 237-265.

Karato, S. (1990) The role of hydrogen diffusivity in the electrical conductivity of the upper mantle. Nature, 347, 272 – 273.

Karato, S. (2006) Influence of hydrogen-related defects on the electrical conductivity and plastic deformation of mantle minerals: a critical review. In Earth's Deep Water Cycle vol. 168, American Geophysical Union, Washington D.C.

Karato, S. (2013) Theory of isotope diffusion in a material with multiple species and its implications for hydrogen-enhanced electrical conductivity in olivine. Physics of Earth Planetary Interiors, 219, 49-54.

Karato, S., and Wang, D. (2013) Electrical conductivity of minerals and rocks. In: Karato, S. (Ed.), Physics and Chemistry of the Deep Earth. Wiley-Blackwell, New York, pp. 145-182.

Karato, S. (2015) Some notes on hydrogen-related point defects and their role in the isotope exchange and electrical conductivity in olivine. Physics of the Earth and Planetary Interiors, 248, 94-98.

Keppler, H., and Bagdassarov, N.S. (1993) High-temperature FTIR spectra of H_2O in rhyolite melt to 1300 °C. American Mineralogist, 78, 1324-1327.

Koch-Müller, M., Matsyuk, S., and Wirth, B. (2004) Hydroxyl in omphacites and omphacitic clinopyroxenes of upper mantle to lower crystal origin beneath the Siberian platform. American Mineralogist, 89, 921-931.

Koch-Müller, M., Speziale, S., Deon, F., Mrosko, M., and Schade, U. (2011) Stress induced proton disorder in hydrous ringwoodite. Physics and Chemistry of Minerals, 38, 65-73.

Kohn, S.C., Brooker, R.V., Frost, D.J., Slesinger, A.E., and Wood, B.G. (2002) Ordering of hydroxyl defects in hydrous wadsleyite (β-Mg_2SiO_4). American Mineralogist, 87, 293-301.

Libowitzky, E. (1999) Correlation of O-H stretching frequencies and O-H…O hydrogen bond lengths in minerals. Monatsh Chem, 130, 1047-1059.

Libowitzky, E., and Beran, A. (2006) The structure of hydrous species in nominally anhydrous minerals: information from polarized IR spectroscopy. Review of

Mineralogy & Geochemistry, 62, 29-52.

Liu, J., Xia, Q.K., Kuritani, T., Hanski, E., and Yu, H.R. (2017) Mantle hydration and the role of water in the generation of large igneous provinces. Nature Communications, 8, 1824.

Liu, W.D., Yang, Y., Zhu, K., and Xia, Q.K. (2018) Temperatue dependecnes of hydrous species in feldspars. Physics and Chemistry of Minerals, https://doi.org/10.1007/s00269-018-0946-1.

Mackwell, S.J., Kohlstedt, D.L., and Paterson, M.S. (1985) The role of water in the deformation of olivine single crystals. Journal of Geophysical Research, 90, 11319 – 11333.

Mackwell, S.J., and Kohlstedt, D.L. (1990) Diffusion of hydrogen in olivine: implications for water in the mantle. Journal of Geophysical Research, 95, 5079-5088.

Nakamoto, K., Margosches, M., and Rundle, R.E. (1955): Stretching frequencies as a function of distances in hydrogen bonds. Journal of the American Chemical Society, 77, 6480-6486.

Padrón-Navarta, J.A., Hermann, J., and O'Neill, H.S.C. (2014) Site-specific hydrogen diffusion rates in forsterite. Earth and Planetary Science Letters, 392, 100-112.

Pandolfo, F., Cámara, F., Domeneghetti, M.C., Alvaro, M., Nestola, F., Karato, S., and Amulele, G. (2015) Volume thermal expansion along the jadeite-diopside join. Physics and Chemistry of Minerals, 42, 1-14.

Panero, W.R., Smyth, J.R., Pigott, J.S., Liu, Z., and Frost, D.J. (2013). Hydrous ringwoodite to 5 K and 35 GPa: Multiple hydrogen bonding sites resolved with FTIR spectroscopy. American Mineralogist, 98, 637-642.

Peslier, A.H., Woodland, A.B., Bell, D.R., and Lazarov, M. (2010) Olivine water contents in the continental lithosphere and the longevity of cratons. Nature, 467, 78-U108.

Purevjav, N., Okuchi, T., Tomioka, T., Wang, X., and Hoffmann, C. (2016) Quantitative analysis of hydrogen sites and occupancy in deep mantle hydrous wadsleyite using single crystal neutron diffraction. Scientific Report, DOI: 10.1038/srep34988.

Purwin, H., Stalder, R., and Skogby, H. (2009) Hydrogen incorporation in Fe- and Na-doped diopsides. European Journal of Mineralogy, 21(4), 691-704.

Padrón, J.A., and Hermann, J. (2017) A Subsolidus Olivine Water Solubility Equation for the Earth's Upper Mantle. Journal of Geophysical Research: Solid Earth, DOI: 10.1002/2017JB014510.

Qin, T., Wentzcovitch R.M., Umemoto, K., Hirschmann, M.M., and Kohlstedt, D.L. (2018) Ab initio study of water speciation in forsterite: Importance of the entropic effect. American Mineralogist, 103, 692-699.

Rossi, G., Oberti, R., Dal, N.A., Molin, G.M., and Mellini, M. (1987) Residual electron density at the M2 site in C2/c clinopyroxenes; relationships with bulk chemistry and sub-solidus evolution. Physics and Chemistry of Minerals, 14, 514-520.

Sakurai, M., Tsujino, N., Tateno, S., Suzuki, T., Yoshino, T., Kawamura, K., and Takahashi, E. (2015) In situ high pressure IR spectroscopic observations on the upper mantle anhydrous minerals using diamond anvil cell. Japan Geoscience Union Meeting.

Shuai, K., and Yang, X.Z. (2017) Quantitative analysis of H-species in anisotropic minerals by polarized infrared spectroscopy along three orthogonal directions. Contributions to Mineralogy and Petrology, 172, 14.

Skogby, H., and Rossman, G.R. (1989) OH^- in pyroxene: An experimental study of incorporation mechanisms and stability. American Mineralogist, 74, 1059-1069.

Skogby, H., Bell, D.R., and Rossman, G.R. (1990) Hydroxide in pyroxene: variations in the natural environment. American Mineralogist, 75, 767-774.

Smyth, J.R., Bell, D.R., and Rossman, G.R. (1991) Incorporation of hydroxyl in upper-mantle clinopyroxenes. Nature, 351, 732-735.

Stalder, R., and Ludwig, T. (2007) OH incorporation in synthetic diopside. European Journal of Mineralogy, 19(3), 373-380.

Thomas, S.M., Bina, C.R., Jacobsen, S.D., and Goncharov, A.F. (2012) Radiative heat transfer in a hydrous mantle transition zone. Earth and Planteary Science Letters, 357, 130-136.

Thoraval, C., Demouchy, S., and Padrón, J.A. (2018) Relative diffusivities of hydrous defects from partially dehydrated natural olivine. Physics and Chemistry of Minerals. DOI: https://doi.org/10.1007/s00269-018-0982-x.

Tian, Z.Z., Liu, J., Xia, Q.K., Ingrin, J., Hao, Y.T., and Christophe, D. (2016) Water concentration profiles in natural mantle orthopyroxenes: A geochronometer for long annealing of xenoliths within magma. Geology, G38620.1

Tielke, J.A., Zimmerman, M.E., and Kohlstedt, D.L. (2017). Hydrolytic weakening in olivine single crystals. Journal of Geophysical Research, 122, 3465-3479.

Tokawai, K., and Nakashima, S. (2010) Dehydration kinetics of muscovite by in situ infrared microspectroscopy. Physics and Chemistry of Minerals, 37, 91-101.

Tollan PME, O'Neill HSC, Hermann J, Benedictus A, and Arculus RJ (2015) Frozen melt-rock reaction in a peridotite xenolith from sub-arc mantle recorded by diffusion of trace elements and water in olivine. Earth and Planetary Science Letters, 422, 169-181.

Wang, D.J., Mookherjee, M., and Xu, Y.S. (2006) The effect of water on the electrical conductivity of olivine. Nature, 443, 977-980.

Withers, A.C., and Behrens, H. (1999) Temperature-induced changes in the NIR spectra of hydrous albitic and rhyolitic glasses between 300 and 100K. Physics and Chemistry of Minerals, 27, 119-132.

Xia, Q.K., Liu, J., Liu, S.C., Kovács, I., Feng, M., and Dang, L. (2013) High water content in Mesozoic primitive basalts of the North China Craton and implications on the destruction of cratonic mantle lithosphere. Earth and Planetary Science Letters, 361, 85-97.

Xu, H., Zhao, Y., Hickmott, D.D., Lane, N.J., Vogel, S.C., Zhang, J., and Daemen, L.L. (2013) High-temperature neutron diffraction study of deuterated brucite. Physics and Chemistry of Minerals, 40, 799-810.

Yang, X.Z., Xia, Q.K., Deloule, E., Dallai, L., Fan, Q.C., and Feng, M. (2008) Water in minerals of the continental lithospheric mantle and overlying lower crust: A comparative study of peridotite and granulite xenoliths from the North China Craton. Chemical Geology, 256, 33-45.

Yang, X.Z., and Keppler, H. (2011) In-situ infrared spectra of OH in olivine to 1100℃. American Mineralogist, 96, 451-454.

Yang, X.Z., and McCammon, C. (2012) Fe^{3+}-rich augite and high electrical conductivity in the deep lithosphere. Geology, 2, 131-134.

Yang, X.Z., Keppler, H., Dubrovinsky, L, and Kurnosov, A. (2014) In-situ infrared spectra of hydroxyl in wadsleyite and ringwoodite at high pressure and high temperature. American Mineralogist, 99, 724-729.

Yang, Y., Xia, Q., Feng, M., and Zhang, P. (2010) Temperature dependence of IR absorption of OH species in clinopyroxene. American Mineralogist, 95, 1439-1443.

Yang, Y., Xia, Q., Feng, M., and Gu, X.Y. (2011) In situ varying temperature FTIR experiment study of rutile. American Mineralogist, 96, 1851-1855.

Yang, Y., Xia, Q., Feng, M., and Liu, S. (2012) OH in nature orthopyroxene: an in situ FTIR investigation at varying temperatures. Physics and Chemistry of Minerals, 39, 413-418.

Yang, Y., Xia, Q., and Zhang, P. (2015) Evolutions of OH groups in diopside and feldspars with temperature. European Journal of Mineralogy, 27, 185-192.

Yoshino, T., Matsuzaki, T., Yamashita, S., and Katsura, T. (2006) Hydrous olivine unable to account for conductivity anomaly at the top of the asthenosphere. Nature, 443, 973-976.

Yoshino, T., Manthilake, G., Matsuzaki, T., and Katsura, T. (2008) Dry mantle transition zone inferred from the conductivity of wadsleyite and ringwoodite. Nature, 451, 326-329.

Yoshino, T., and Katsura, T. (2013) Electrical conductivity of mantle minerals: role of water in conductivity anomalies. Annual Review of Earth and Planetary Sciences, 41, 605-628.

Zhao, C.C., and Yoshino, T. (2016) Electrical conductivity of mantle clinopyroxene as a function of water content and its implication on electrical structure of uppermost mantle. Earth and Planetary Science Letters, 447, 1-9.

Zhang, M., Hui, Q., Lou, X.J., Redrern, S.A.T., Salje, E.K.H., and Tarantino, S.C. (2006) Dehydroxylation, proton migration, and structural changes in heated talc: An infrared spectroscopic study. American Mineralogist, 91, 816-825.

Zhang, M., Salje, E. K. H., Carpenter, M. A., Wang, J.Y., Groat, L. A., Lager, G. A., Wang, L., Beran, A., and Bismayer, U. (2007) Temperature dependence of IR absorption of hydrous/hydroxyl species in minerals and synthetic materials. American Mineralogist, 92, 1502-1517.

Zhang, M., Tarantino, S.C., Su, W., Lou, X., and Ren, X. (2016) Phonons, OH vibrations ans structural modifications of phlogopite at high temperatures: an in-situ infrared spectroscopic study. American Mineralogist, 101, 1873-1883.

Figure captions

FIGURE 1.Unpolarized FTIR spectra of OH in the ten clinopyroxenes at room temperature. The spectra are shifted for clarity. The positions of the four groups OH bands are indicated by dotted lines: red lines indicate the group 1 OH; blue lines indicate the group 2 OH; green lines indicate the group 2 OH; black lines indicate the

group 4 OH.

FIGURE 2. Relationship between OH frequencies and chemical compositions in the clinopyroxenes: (a) Wavenumbers of the group 1 OH band as a function of tetrahedral coordinated Al^{3+} content in atoms per formula unit (a.p.f.u.). The data of diopside (YT-25, peridotite) is from Hao et al. (2016), the data of diopside (NS-16, peridotite) and diopside (NS-29, peridotite) are from Yang et al. (2008). The data of augite and diopside (GRR04, granulite) are unpublished data; (b) Wavenumbers of the group 2a OH band as a function of tetrahedral coordinated Al^{3+} content in atoms per formula unit (a.p.f.u.); (c) Wavenumbers of the group 2b OH band as a function of M vacancies; (d) Wavenumbers of the group 3 OH band as a function of M vacancies. The M vacancy is a first approximation since the calculation is very simple neglecting Fe^{3+}.

FIGURE 3. In situ unpolarized FTIR spectra of OH in the ten clinopyroxenes at high temperatures. The room-temperature positions of the OH bands are indicated by dotted lines. The arrow indicates the appearance of the new band at 3443 cm^{-1} in the diopside-Austria and diopside-Aksu2. The spectra are shifted for clarity.

FIGURE 4. Plots of frequency of the OH bands of clinopyroxenes against temperature: (a) group 1; (b) group 2a; (c) group 2b; (d) group 3; (e) group 4

FIGURE 5. Variation of the integral absorbances of the OH bands with temperature: (a) The bulk integral absorbances; (b) The individual integral absorbance of each OH band. The dotted lines indicate the turning points at which dehydration starts.

FIGURE 6. Room-temperature unpolarized FTIR spectra of the samples annealed in N_2 at 1000°C.

FIGURE 7. Hydrogen diffusivities during dehydration as a function of Fe and ^{IV}Al content in atoms per formula unit (a.p.f.u.): (a) Bulk and site-specific hydrogen diffusivities vs. Fe content; (b) Bulk and site-specific hydrogen diffusivities vs. ^{IV}Al content; (c) Bulk hydrogen diffusivities vs. Fe content excluding the diopside-Austria; (d) Bulk hydrogen diffusivities vs. ^{IV}Al content excluding the diopside-Austria.

FIGURE 8. Unpolarized NIR spectra of the samples normalized to 1 cm of thickness before and after dehydration. The arrows indicate the absorptions of Fe^{2+}.

FIGURE 9. (a) Relationship between temperature dependence of OH frequency shift and room-temperature frequency. The blue symbols are the data from this study and the black symbols are the data from the literature. (b) Correlation between O-H stretching frequency and O-H…O distance of the four groups of OH. The black symbols indicate the data at room temperature, and the blue symbols indicate the data at 1000 ^oC. For each group of OH in the ten samples, the highest and lowest frequencies were chosen. (c) The comparison of ranges of O-H…O distance of the four groups of OH between room temperature and 1000 ^oC.

FIGURE 10. (a) Unpolarized FTIR spectra of OH in the diopside from Austria recorded at room temperature before heating and after annealing at 800 and 900 ^oC for different time. The dotted lines indicate the new band at 3443 cm^{-1}. The spectra are shifted for clarity. (b) Room-temperature polarized FTIR spectra of OH in diopside from Austria after annealing at 900 ^oC for 30 min with polarizer rotating 0^o and 90^o. (c) Plots of integral absorbance of the deconvoluted OH bands of the diopside from Austria against annealing time at 800 ^oC (integral absorbance of the FTIR spectrum before heating was used as the initial value). (d) Integral absorbance of the deconvoluted OH bands of the diopside from Austria against annealing time at 900 ^oC.

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Table 1 Cation proportions as calculated from electron microprobe analyses of clinopyroxenes.

	Diopside-Austria	Diopside-marble	Diopside-JD	Augite-YFL	Omphacite	Diopside-Aksu	Diopside-Russia	Diopside-deep sea	Augite-NS
K	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Na	0.003	0.001	0.135	0.119	0.232	0.001	0.023	0.033	0.122
Cr	0.000	0.000	0.023	0.000	0.002	0.000	0.017	0.033	0.000
Ca	0.992	1.010	0.776	0.653	0.676	1.016	0.952	0.871	0.648
Mg	0.888	0.896	0.782	0.706	0.717	0.929	0.930	0.828	0.818
Mn	0.006	0.003	0.003	0.004	0.002	0.004	0.001	0.002	0.003
Ti	0.001	0.003	0.014	0.030	0.003	0.000	0.003	0.005	0.023
Al	0.011	0.088	0.301	0.469	0.185	0.009	0.009	0.298	0.389
Ni	0.001	0.001	0.002	0.001	0.002	0.001	0.001	0.000	0.000
Fe	0.076	0.043	0.089	0.300	0.195	0.072	0.043	0.085	0.223
Si	2.000	1.955	1.883	1.756	2.002	1.982	2.009	1.846	1.808
Total	3.978	4.000	4.008	4.038	4.016	4.014	3.988	4.001	4.034
^{IV}Al	0.000	0.045	0.117	0.244	0.000	0.018	0.000	0.154	0.192
^{VI}Al	0.011	0.043	0.184	0.225	0.185	-0.009	0.009	0.144	0.197
Vacancies	0.022	0.000	-0.008	-0.038	-0.016	-0.014	0.012	-0.001	-0.034

Note: The total Fe was calculated as FeO. The error of multi-point analysis is <1% for elements with concentration >5% and <3% for elements with concentration >1%. The cations were calculated based on 6 oxygen atoms except for the data for diopside (marble) which were from Johnson et al. (2002). The vacancies were calculated as 4 minus total cations per 6 oxygen atoms. The diopside-Aksu1 and diopside-Aksu2 have the same chemical composition, labeled as diopside-Aksu in the table.

Table 2 Bulk and site-specific hydrogen diffusivities

Sample	Thickness (mm)	Temperature (°C)	Site-specific diffusivity ($log_{10}D$)						Bulk diffusivity ($log_{10}D$)
			Peak position (cm^{-1})						
			3640	3620	3540	3520	3450	3360	
Diopside-Russia	0.866	1000	-12.40 *±0.60*	-12.15 *±0.54*	/	-12.10 *±0.30*	-12.15 *±0.54*	/	-12.15 *±0.24*
Diopside-marble	0.212	1000	-12.30 *±0.30*	/	-12.00 *±0.22*	/	/	/	-12.22 *±0.18*
Diopside-JD	0.166	1000	-11.80 *±0.20*	/	-11.92 *±0.22*	/	-11.74 *±0.18*	/	-11.92 *±0.18*
Diopside-deep sea	0.146	1000	-11.70 *±0.30*	/	-12.00 *±0.22*	/	-11.74 *±0.18*	/	-12.00 *±0.26*
Augite-NS	0.980	1000	-11.30 *±0.30*	/	-11.10 *±0.20*	/	-11.52 *±0.48*	/	-11.22 *±0.18*
Diopside-Austria	0.759	1000	-10.60 *±0.22*	/	/	/	-10.70 *±0.30*	-10.55 *±0.19*	-10.80 *±0.20*

Figure 1

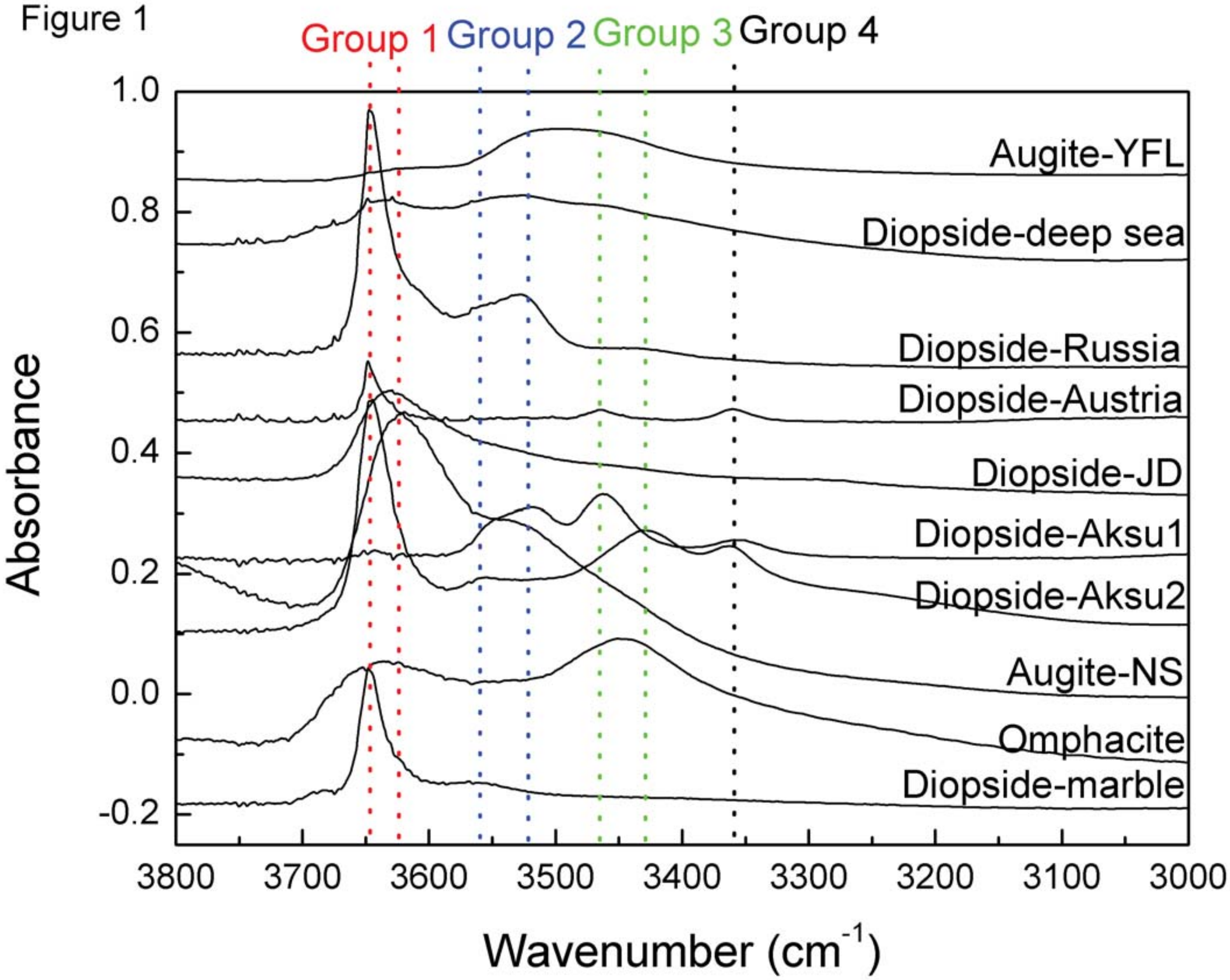
Group 1
Group 2
Group 3
Group 4
Absorbance
1.0
0.8
0.6
0.4
0.2
0.0
-0.2
Augite-YFL
Diopside-deep sea
Diopside-Russia
Diopside-Austria
Diopside-JD
Diopside-Aksu1
Diopside-Aksu2
Augite-NS
Omphacite
Diopside-marble
3800
3700
3600
3500
3400
3300
3200
3100
3000
Wavenumber (cm^{-1})

Figure 2

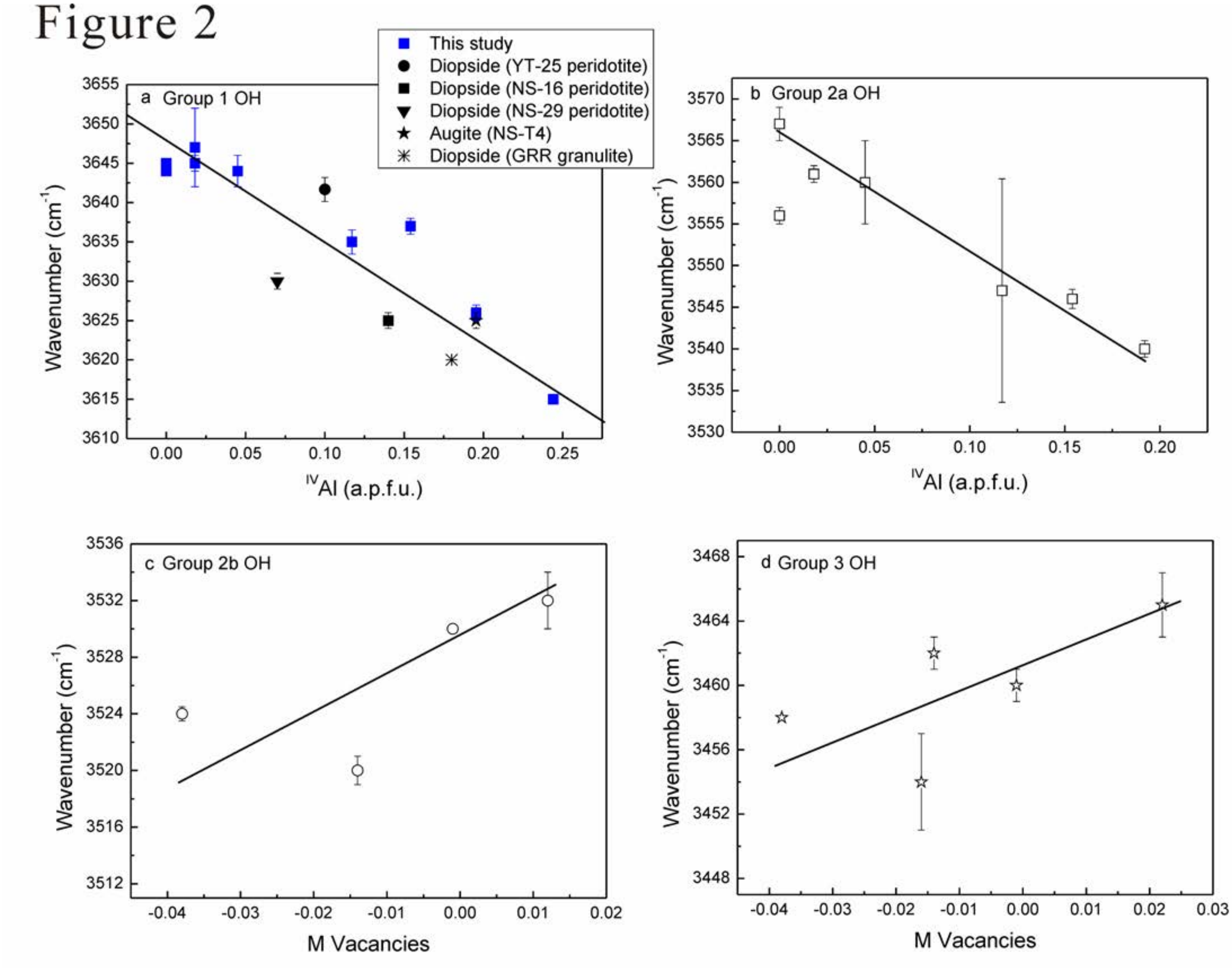
This study
Diopside (YT-25 peridotite)
Diopside (NS-16 peridotite)
Diopside (NS-29 peridotite)
Augite (NS-T4)
Diopside (GRR granulite)
a Group 1 OH
Wavenumber (cm-1)
IVAl (a.p.f.u.)
b Group 2a OH
Wavenumber (cm-1)
IVAl (a.p.f.u.)
c Group 2b OH
Wavenumber (cm-1)
M Vacancies
d Group 3 OH
Wavenumber (cm-1)
M Vacancies

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Figure 3

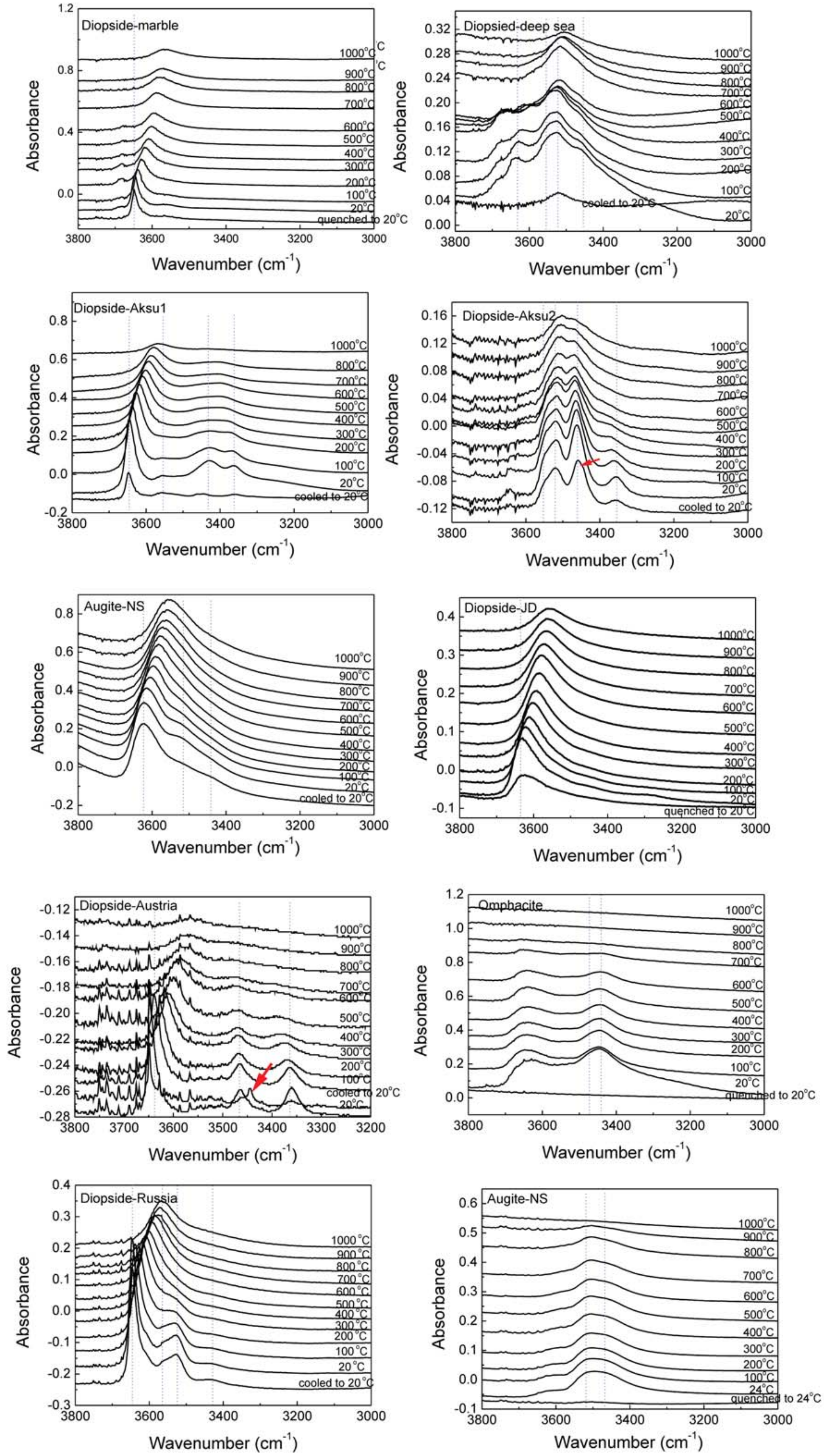

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Figure 4

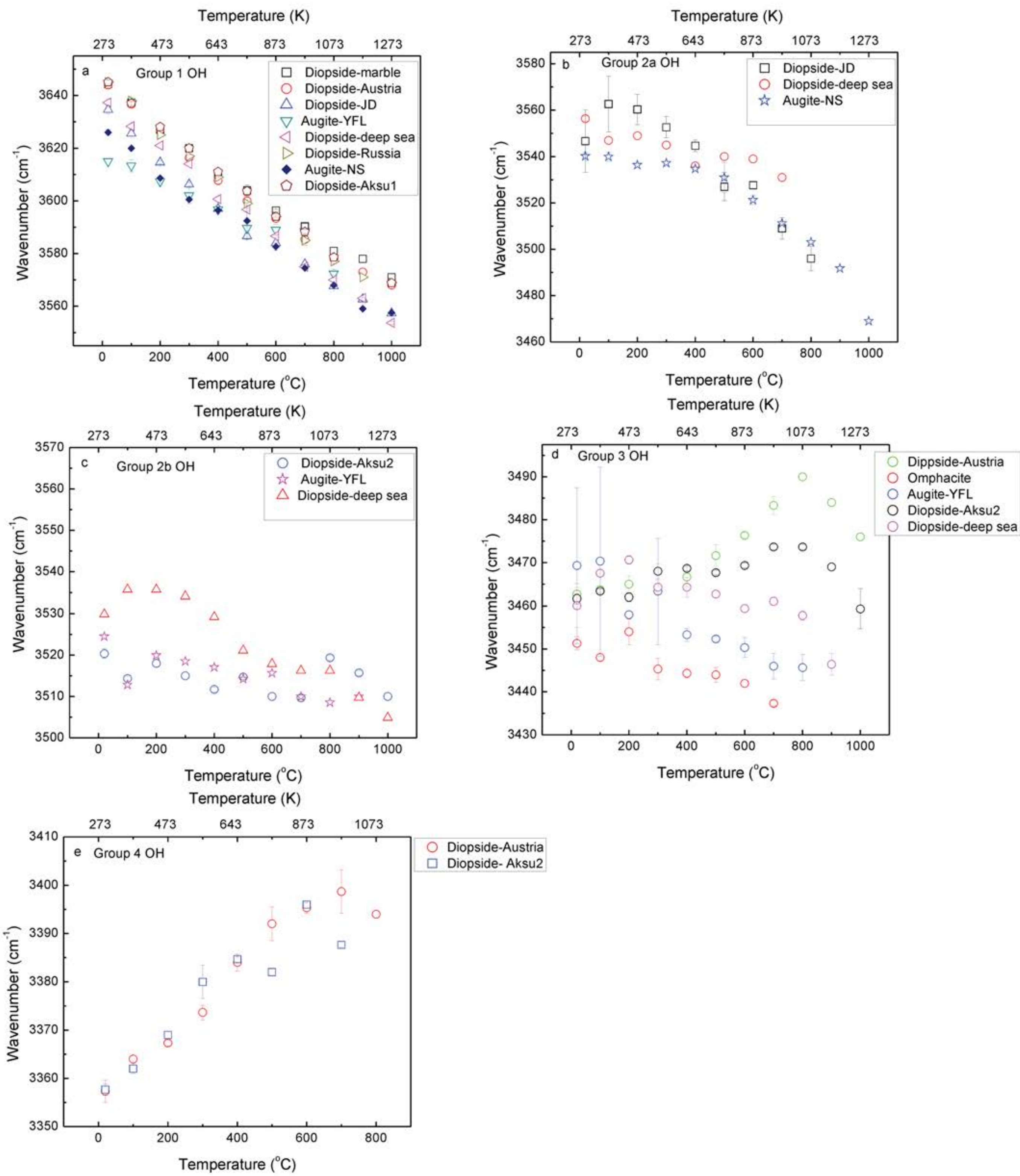

Figure 5

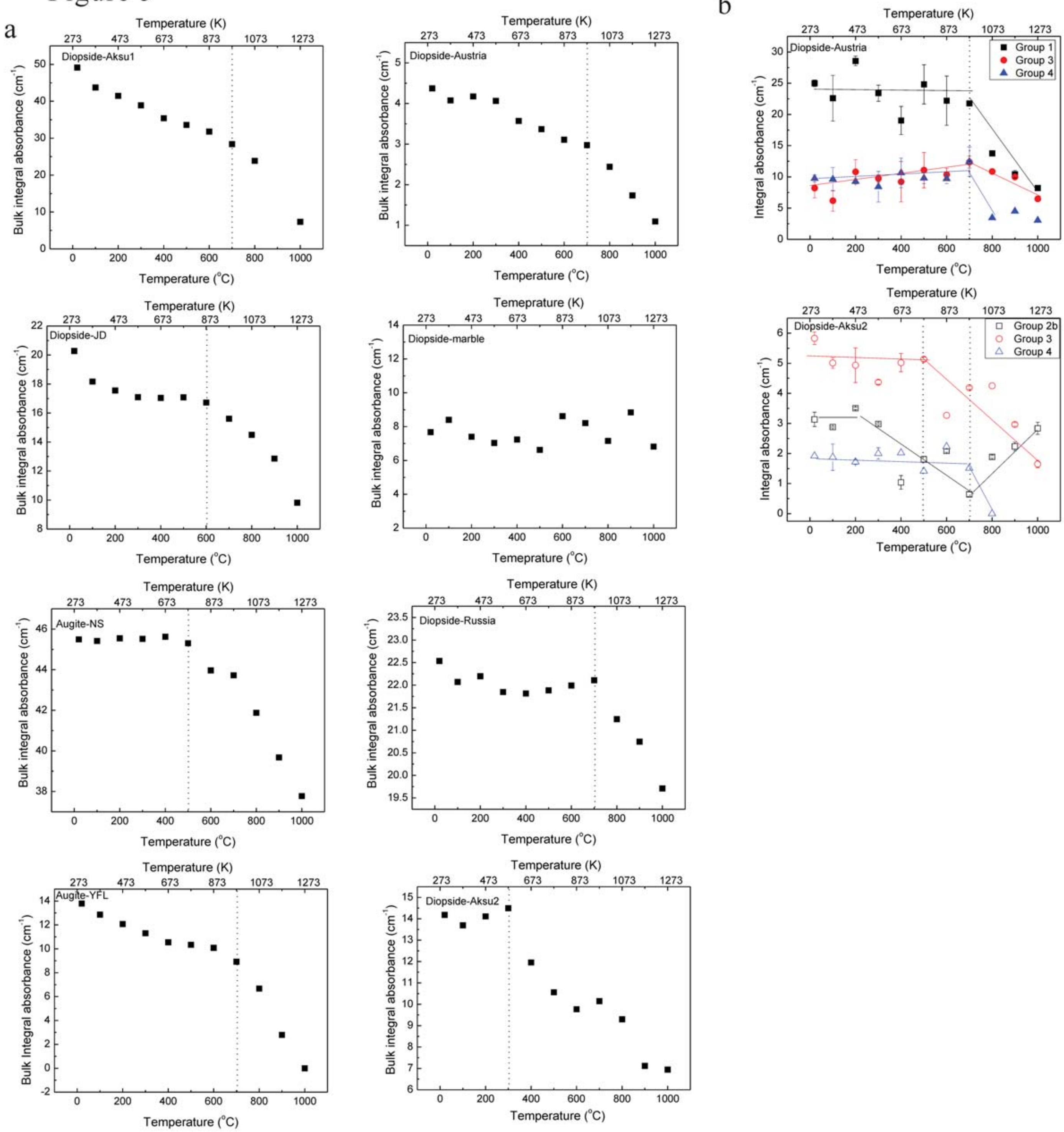
a
b
Temperature (K)
Temperature (°C)
Bulk integral absorbance (cm⁻¹)
Integral absorbance (cm⁻¹)
Diopside-Aksu1
Diopside-Austria
Diopside-JD
Diopside-marble
Augite-NS
Diopside-Russia
Augite-YFL
Diopside-Aksu2
Group 1
Group 2b
Group 3
Group 4

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Figure 6

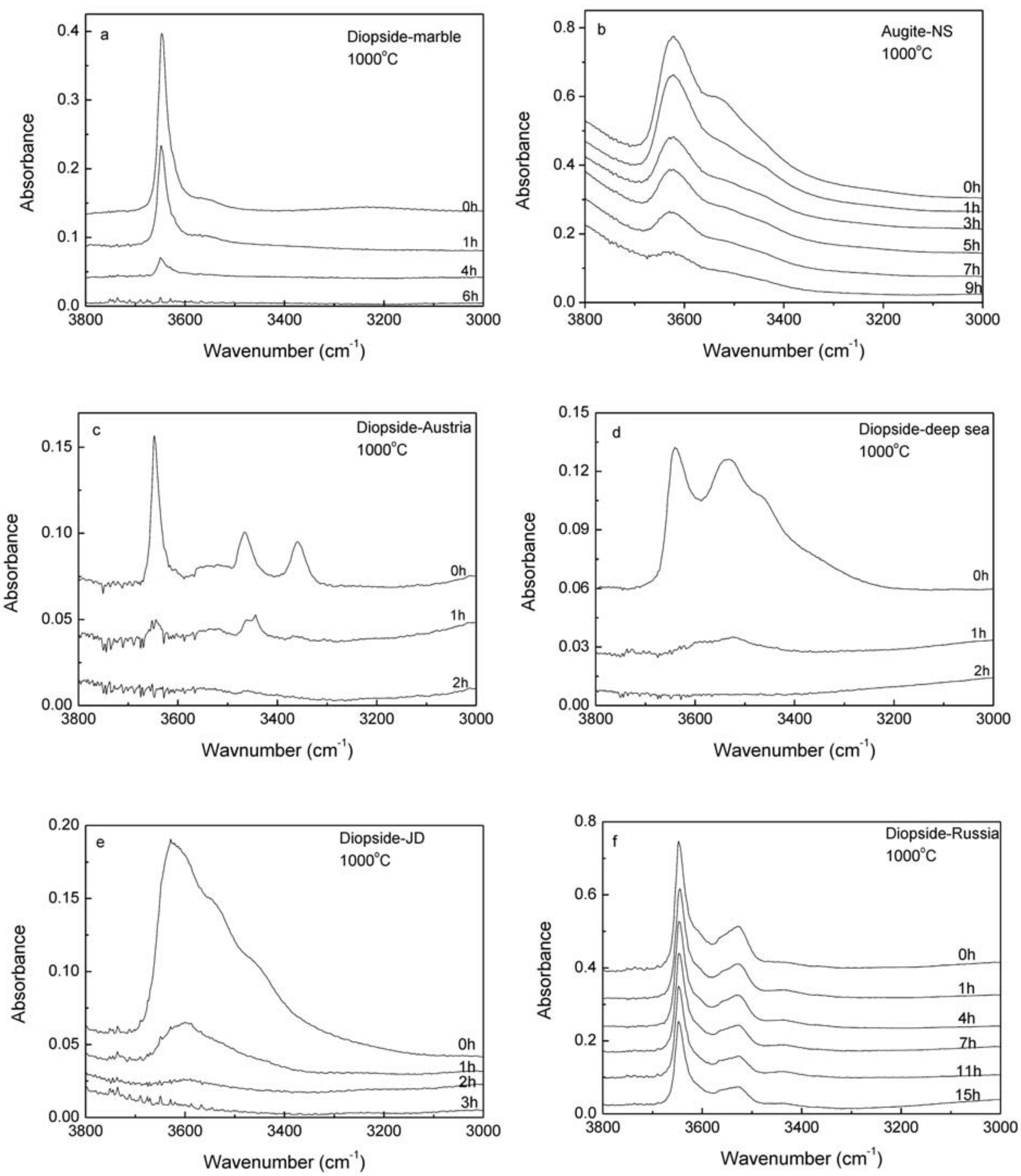

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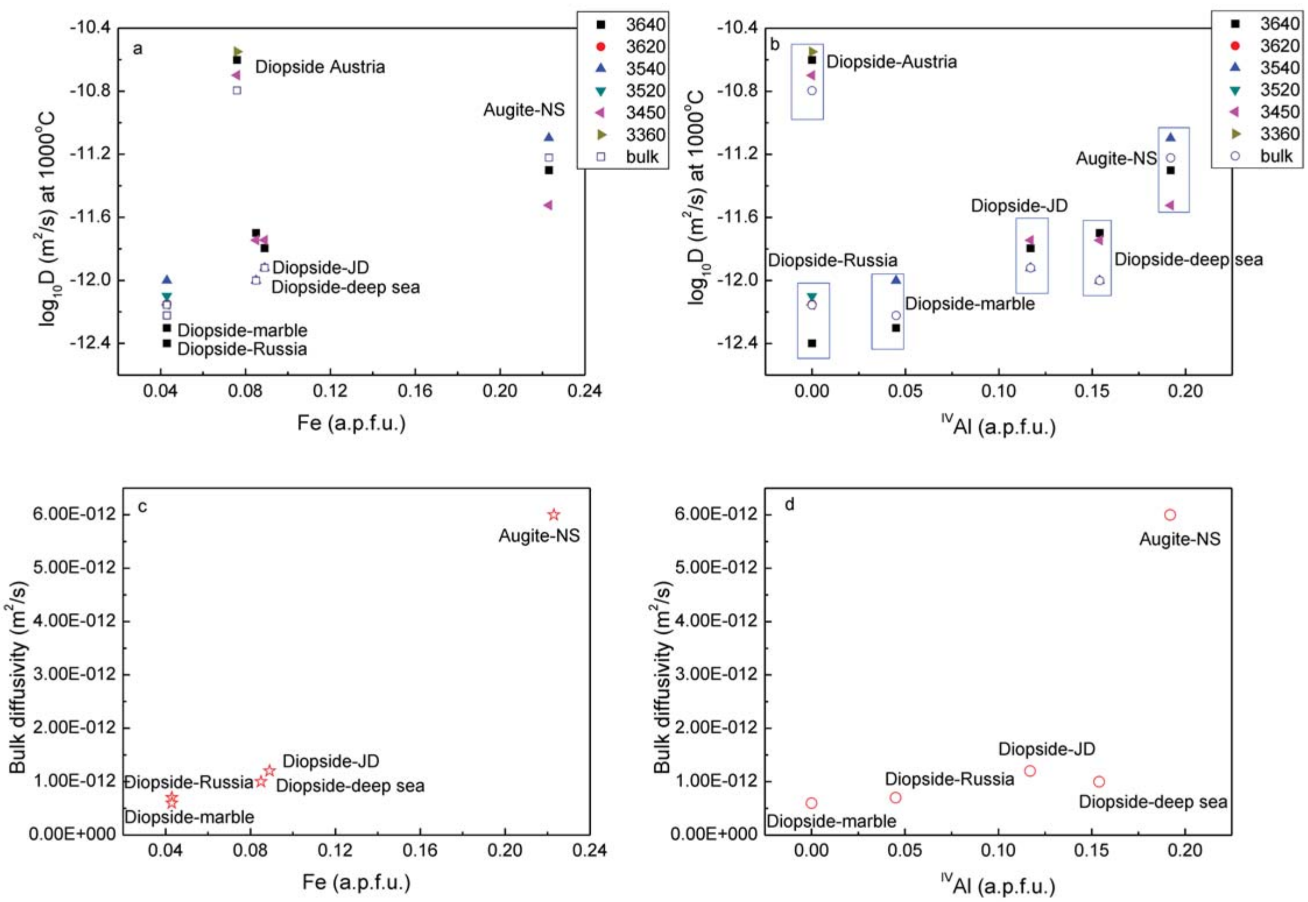
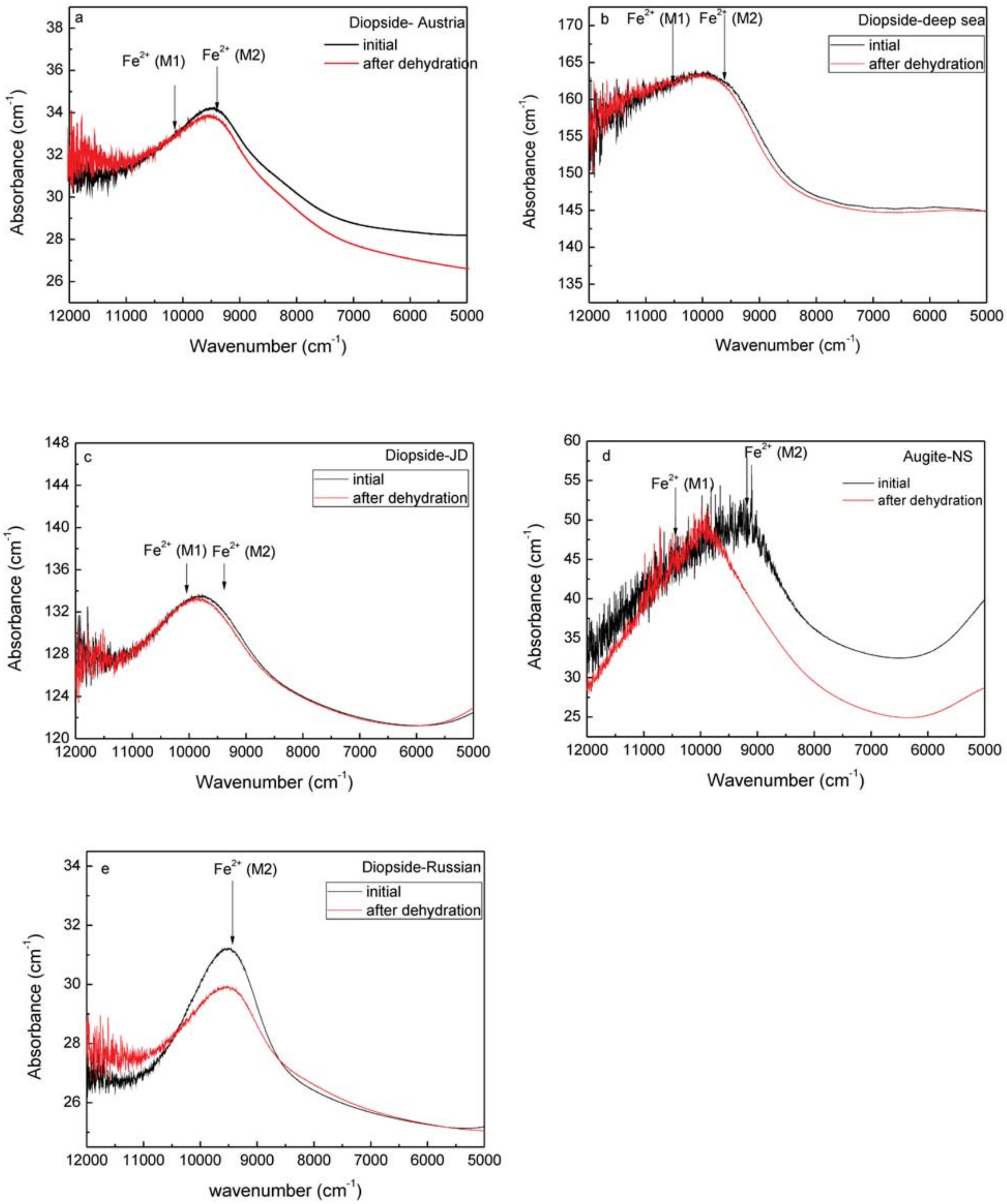
Figure 7



DOI: https://doi.org/10.2138/am-2019-6661

Figure 8



DOI: https://doi.org/10.2138/am-2019-6661

Figure 9

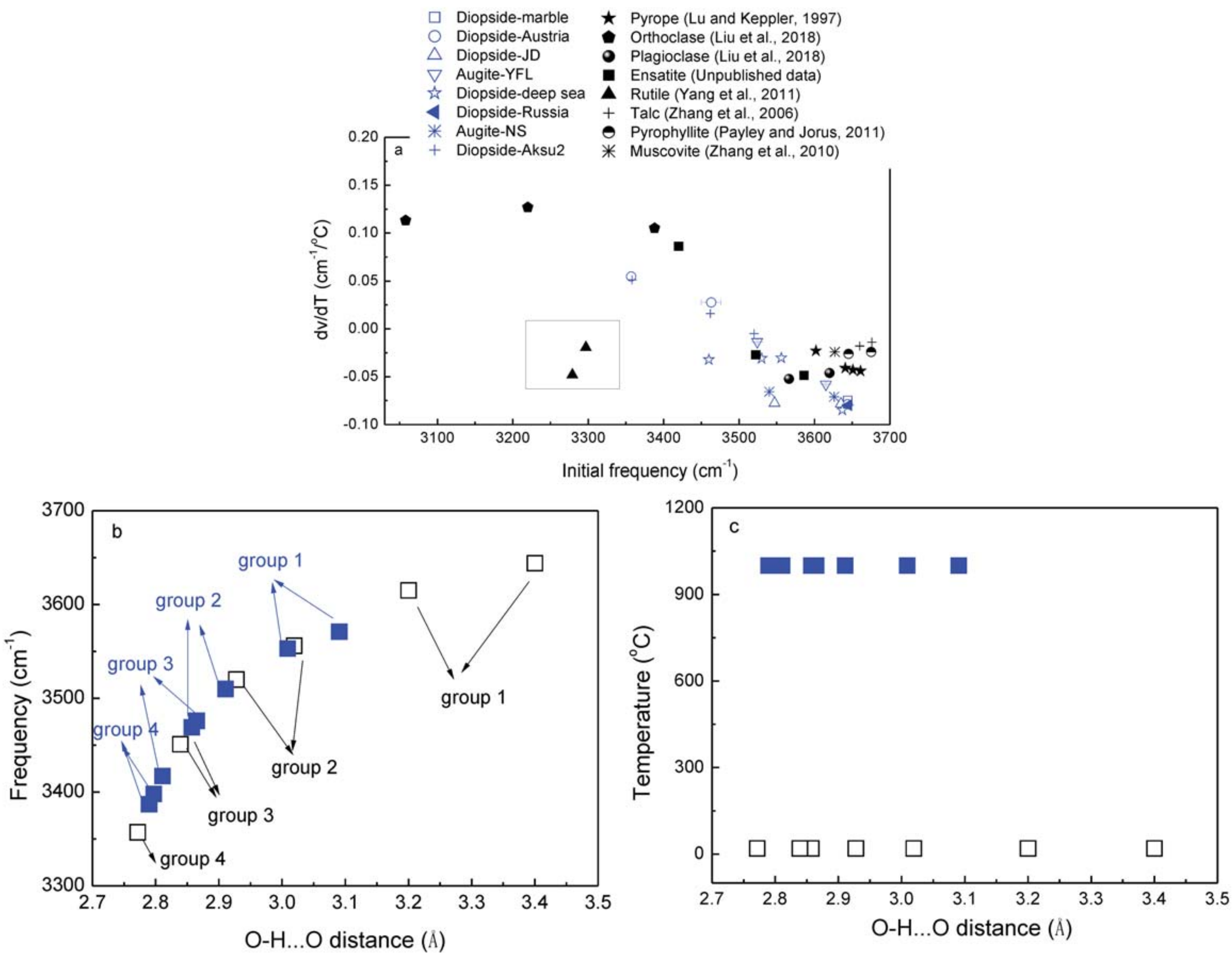


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Figure 10