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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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 °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 °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 Fe²⁺. For two diopsides with a mantle affinity, the diffusivity is about 10⁻¹² m²/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;
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 diopside-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%.
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 Continuum 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$^{-1}$ (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 °C. For the diopside-Aksu 2, the absorbances of the bands of group 3 and group 4 do not change until increasing temperature to 500 and 700 °C, respectively, while the absorbance of the group 2b band decrease first then increase with increasing temperature to 700 °C.

**Hydrogen diffusivities at 1000°C**

To investigate dehydration at high temperature, we conducted dehydration experiments at 1000 °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 (6-7×10⁻¹³ m²/s), moderate in the diopsides from mantle peridotite (diopside-deep sea and
diopside-JD) \( (1 \times 10^{-12} \text{ m}^2/\text{s}) \), and the fastest in the diopside-Austria and augite-NS \( (6 \times 10^{-12} \text{ m}^2/\text{s}) \). 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 \(^{IV}\text{Al}\) contents. The diffusivity of the group 1 OH is more correlated with \(^{IV}\text{Al}\) content, while that of the group 2 OH is more correlated with Fe content. The bulk hydrogen diffusivity is more correlated with Fe than \(^{IV}\text{Al}\) 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 °C 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 °C.
(Figure 9b). For the group 1 OH with frequencies around 3571-3553 cm$^{-1}$ at 1000 °C, the predicted O-O distance is about 3.0 Å. For the group 2 OH with frequencies around 3510-3469 cm$^{-1}$ at 1000 °C, 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 °C, 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 °C, the predicted O-O distance is about 2.8 Å. Obviously, the O-O distances for the four groups OH at 1000 °C are more centralized than those observed at room temperature (Fig. 9c). Thus, the one broad band at high temperature such as 1000 °C 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 ($\varepsilon$ 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
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
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 °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$^{2+}$: $2Fe^{2+} + OH^- = Fe^{3+} + O^{2-} + 1/2H_2$. 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 °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 \textit{in situ} high temperature and high pressure FTIR spectroscopic investigations have to be carried out.

\textbf{Preservation of hydrogen speciation and content in quenched clinopyroxene}

Our \textit{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 \textsuperscript{IV}Al contents in the clinopyroxene samples. Thus, for clinopyroxene samples with high Fe and \textsuperscript{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 °C 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., \(6\times10^{-12}\), \(1.3\times10^{-11}\), and \(3.1\times10^{-11}\) m\(^2\)/s at 1100°C, 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 $1 \times 10^{-12}$ and $1.2 \times 10^{-12}$ m$^2$/s at 1000 °C in the two diopsides from mantle peridotites, two orders of magnitude lower than $4 \times 10^{-10}$ m$^2$/s in mantle olivine (Mackwell and Kohlstedt 1990), and slightly lower than $4 \times 10^{-12}$ 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 $1 \times 10^{-12}$ m$^2$/s at 1000 °C 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 °C of the group 1 OH (3640 cm$^{-1}$, with the hydrogen diffusivity of $1.6 \times 10^{-12}$) is slightly higher than that of the group 2 OH (3540 cm$^{-1}$, with the hydrogen diffusivity of $1.2 \times 10^{-12}$). 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.

ACKNOWLEDGMENTS

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Mineralogy & Geochemistry, 62, 29-52.


Yang, Y., Xia, Q., and Zhang, P. (2015) Evolutions of OH groups in diopside and...


**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 °C. 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 °C.

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 °C 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 °C for 30 min with polarizer rotating 0° and 90°. (c) Plots of integral absorbance of the deconvoluted OH bands of the diopside from Austria against annealing time at 800 °C (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 °C.
Table 1 Cation proportions as calculated from electron microprobe analyses of clinopyroxenes.

<table>
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<tr>
<th></th>
<th>Diopside-Austria</th>
<th>Diopside-marble</th>
<th>Diopside-JD</th>
<th>Augite-YFL</th>
<th>Omphacite</th>
<th>Diopside-Aksu</th>
<th>Diopside-Russia</th>
<th>Diopside-deep sea</th>
<th>Augite-NS</th>
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<td>0.000</td>
<td>0.000</td>
<td>0.000</td>
<td>0.000</td>
<td>0.000</td>
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<td>-0.014</td>
<td>0.012</td>
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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>
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<th>Sample</th>
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<th>Site-specific diffusivity (log_{10}D)</th>
<th>Bulk diffusivity (log_{10}D)</th>
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</table>
Figure 1

Absorbance

Group 1, Group 2, Group 3, Group 4

Augite-YFL
Diopside-deep sea
Diopside-Russia
Diopside-Austria
Diopside-JD
Diopside-Aksu1
Diopside-Aksu2
Augite-NS
Omphacite
Diopside-marble

Wavenumber (cm⁻¹)

3800 3700 3600 3500 3400 3300 3200 3100 3000
Figure 2

(a) Group 1 OH

(b) Group 2a OH

(c) Group 2b OH

(d) Group 3 OH

Wavenumber (cm⁻¹)

IVAl (a.p.f.u.)

M Vacancies

Wavenumber (cm⁻¹)

This study
• Diopside (YT-25 peridotite)
• Diopside (NS-16 peridotite)
• Diopside (NS-20 peridotite)
• Augite (NS-T4)
• Diopside (GRR granulite)

Always consult and cite the final, published document. See http://www.minsocam.org or GeoscienceWorld
Figure 3

Diopside-marble

Absorbance

Wavenumber (cm\(^{-1}\))

Diopside-deep sea

Absorbance

Wavenumber (cm\(^{-1}\))

Diopside-Aksu1

Absorbance

Wavenumber (cm\(^{-1}\))

Augite-NS

Absorbance

Wavenumber (cm\(^{-1}\))

Diopside-JD

Absorbance

Wavenumber (cm\(^{-1}\))

Omphacite

Absorbance

Wavenumber (cm\(^{-1}\))

Diopside-Austria

Absorbance

Wavenumber (cm\(^{-1}\))

Diopside-Russia

Absorbance

Wavenumber (cm\(^{-1}\))

Augite-NS

Absorbance

Wavenumber (cm\(^{-1}\))
Figure 4

(a) Group 1 OH
- Diopside-marble
- Diopside-Austria
- Diopside-JD
- Augite-YFL
- Diopside-deep sea
- Augite-Russia
- Augite-NS
- Diopside-Aksu1

(b) Group 2a OH
- Diopside-JD
- Diopside-deep sea
- Augite-NS

(c) Group 2b OH
- Diopside-Aksu2
- Augite-YFL
- Diopside-deep sea

(d) Group 3 OH
- Diopside-Austria
- Omphacite
- Augite-YFL
- Diopside-Aksu2
- Diopside-deep sea

(e) Group 4 OH
- Diopside-Austria
- Diopside-Aksu2
Figure 5
Figure 6
Figure 7
Figure 8
Figure 9
Figure 10

(a) Absorbance spectra before and after heating at different temperatures and times. (b) Spectra with additional peaks at 50°C. (c) Integral absorbance vs. time for annealing at 800°C. (d) Integral absorbance vs. time for annealing at 900°C.