Quantitative analysis of H-species in anisotropic minerals by unpolarized infrared spectroscopy: an experimental evaluation

YANGYANG QIU¹, HAOTIAN JIANG¹, KOVÁCS ISTVÁN², QUN-KE XIA³, AND XIAOZHI YANG¹,*

¹ State Key Laboratory for Mineral Deposits Research, School of Earth Sciences and Engineering, Nanjing University, Nanjing 210023, PR China
² Research Centre for Astronomy and Earth Sciences, Hungarian Academy of Sciences, H-1112 Budapest, Hungary
³ Institute of Geology and Geophysics, School of Earth Sciences, Zhejiang University, Hangzhou 310027, PR China
*: corresponding author (xzyang@nju.edu.cn)

ABSTRACT

Appreciated attempts have been devoted to use a simple unpolarized infrared analysis on unoriented anisotropic crystals of nominally anhydrous minerals to determine the content of H-species, rather than using the more demanding polarized techniques which determine the true contents of H-species (given that a reliable calibration coefficient is available). In this context, different approaches have been either empirically or theoretically proposed for the quantification; however, the involved accuracy has not been systematically documented.
by experimental work of both polarized and unpolarized analyses. In this study, we present a careful evaluation of this issue by conducting experimental measurements on a series of gem-quality OH-bearing olivine, clinopyroxene and orthopyroxene single crystals. The samples were carefully prepared for polarized and unpolarized infrared analyses, and the obtained spectra were used to estimate the H$_2$O contents. We show that, regardless the applied protocol, a single unpolarized determination is inadequate for quantitative analysis and the uncertainty could be up to ~80%. The unpolarized method of Paterson (1982), by considering the linear absorbance intensity either through a single analysis or by averaging the data from multi-grain analyses, commonly underestimates the H$_2$O content, by a factor of up to ~6. The other unpolarized calibration method by using the averages of integrated absorbances of unoriented grains is in general of good accuracy, mostly within ±25% even for analyses on 2 grains (with perpendicular indicatrix sections), and the accuracy is even better if as many as 10 gains of random orientations are involved, e.g., within ±10%. Therefore, the latter method may be safely applied to quantify H in anisotropic minerals if a reasonable number of randomly oriented grains are chosen for the analyses. However, the uncertainty is non-systematic, in that it could underestimate but could also overestimate the contents depending on the orientations of the studied unoriented grains. The results lay a solid basis for quantifying H-species in anisotropic minerals and for documenting the quantitative effect of H on the physical properties of the host phases.

**Keywords:**

OH groups; Quantitative analysis; Unpolarized spectroscopy; Infrared spectroscopy;
Nominally anhydrous minerals

**INTRODUCTION**

The importance of water for the origin and evolution and life on Earth and even the Earth itself makes it an intriguing topic in Earth Sciences. Water in the Earth is rarely present as H$_2$O molecules (e.g., as seen in the oceans), but is most abundant in the form of hydrogen (H) incorporated in the lattice of various minerals of the planet’s interior. In the past decades, H in nominally anhydrous minerals, the dominant constituents of the crust and mantle, has received increasing interest, due to the widespread recognition of the disproportionate importance of even trace amounts of H in governing Earth's geochemical evolution, geophysical properties and geodynamics (Keppler and Smyth 2006; Yang et al. 2014a; Demouchy and Bolfan-Casanova, 2016; Peslier et al., 2017; Xía et al., 2017). In particular, partial melting, element partitioning, ionic diffusion, mechanical strength and electrical conductivity could be affected by small amounts of H in the host minerals (e.g., Inoue 1994; Righter and Drake 1999; Mei and Kohlstedt 2000; Regenauer-Lieb et al. 2001; Hier-Majumder et al. 2005; Huang et al. 2005; Green et al., 2010; Kovács et al., 2012; Yang et al. 2011, 2012; Yang 2012). The effect of H on these aspects, as well as the partitioning, distribution and storage of water inside the Earth, is closely linked to its amount and speciation types, of which the latter is related to the incorporation mechanism. H is structurally present in several forms such as OH groups, molecular H$_2$O and molecular H$_2$ (Keppler and Smyth 2006; Yang et al. 2016), and OH groups in nominally anhydrous minerals have attracted particular interest, because the formation involves modification of
silicate matrix of the host structure (e.g., by breaking strong Si-O bond and/or creating
vacancies). Therefore, the key in many cases is to determine accurately the concentration
and species of H.

Fourier-transform infrared (FTIR) spectroscopy is a very powerful technique, and remains
the most widely applied method, for probing H in nominally anhydrous minerals, because
of its extreme sensitivity to H, inexpensive costs and non-destructive analyses. Also, it can
be easily carried out in situ on very small sample domains, and distinguishes readily
different types of H-species such as OH groups, inclusion H₂O, molecular H₂ and organic
hydrogen. Moreover, information on the orientations of H in the host structure and on the
lengths of hydrogen bond could be deduced if polarized radiation is used, and the exact
amount of H can be calculated if an externally determined mineral-specific IR calibration
coefficient is available. Accordingly, considerable effort in the past decades has been
devoted to develop a simple yet accurate method for measuring the concentration of H in
nominally anhydrous minerals with FTIR spectroscopy (e.g., Dowty 1978; Paterson 1982;
Libowitzky and Rossman 1996; Asimow et al. 2006; Kovács et al. 2008; Withers 2013;
Shuai and Yang 2017). The difficulty involves mainly optically anisotropic minerals and
very small grains, where particular attention has been focused on the measurements using
polarized or unpolarized analyses. In general, polarized analysis is more demanding than
unpolarized work, concerning both sample preparation and FTIR determinations. The
general principle of unpolarized FTIR spectroscopy has been theoretically documented,
with some key assumptions made in the mathematical deductions (e.g., Kovács et al. 2008;
Some preliminary studies have been conducted on testing the accuracy of the unpolarized methodology (e.g., Bali et al. 2008; Kovács et al. 2008; Sambridge et al. 2008; Férot and Bolfan-Casanova 2012; Sokol et al. 2013; Withers 2013; Padron-Navarta et al. 2014; Bizimis and Peslier 2015). However, it should be pointed out that the available work has been conducted with only one or just a few samples and/or under the assumption that calculated absorbance with numerical approximations is reliable in reflecting sample true H content. A detailed and comprehensive experimental test of the unpolarized methodology, in particular how accurate the result could be, has not yet been reported.

In this work, we have carried out a detailed experimental evaluation for the quantification of H-species in anisotropic minerals by both polarized and unpolarized FTIR spectrometry. The work is based on a direct comparison between the measured true contents by polarized method and the determined values by unpolarized method, differing from some available studies where the true contents were produced for example by synthesizing the axis-related polarized spectra or by matching the spectra of silicate overtone bands of the samples with those of reported oriented samples (e.g., Bali et al., 2008; Férot and Bolfan-Casanova 2012; Padron-Navarta et al. 2014), and this would make the evaluation more straightforward. The studied samples include a series of gem-quality olivine (Ol), clinopyroxene (Cpx) and orthopyroxene (Opx) single crystals. These crystals, naturally derived and experimentally H-annealed, are characterized by a range of H$_2$O contents from less than 30 to more than 400 ppm H$_2$O. We first present a brief technical introduction of the polarized and
unpolarized methods, and then report a careful evaluation of the H quantification by unpolarized analyses.

**BACKGROUND**

The quantitative measurements of H concentration by FTIR spectroscopy are based on the modified version of the Beer-Lambert law:

\[ c = \frac{Abs}{\varepsilon \cdot t} \]  

(1)

where \( c \) is the content of H-species (usually expressed as the equivalent content of H\(_2\)O by weight), \( Abs \) is the integrated absorbance in the interested region (cm\(^{-1}\), e.g., usually 3700 to 2800 cm\(^{-1}\) for OH groups), \( \varepsilon \) is the calibration coefficient, and \( t \) is the thickness of the sample in cm. Therefore, the H content is simply a function of the integrated absorbance normalized to 1 cm thickness (\( Abs_{\text{total}} \)), given that the calibration coefficient is already known, and Eq (1) becomes

\[ c = \frac{Abs_{\text{total}}}{\varepsilon} \]  

(2)

For optically anisotropic minerals, the determined intensity of H-species depends strongly on the orientation of the infrared-active dipole relative to the incident radiation, and \( Abs_{\text{total}} \) is then the sum of the thickness-normalized integrated absorbance along the three principal axes (\( X, Y \) and \( Z \)), which are obtained by three polarized FTIR spectra with incident light polarized along the three axes, respectively:

\[ Abs_{\text{total}} = Abs_X + Abs_Y + Abs_Z \]  

(3)

This requires orienting single crystals along some fundamental planes, so that the principal
axes can be determined. However, performing such a procedure on small crystals, either natural or synthetic, is usually hard and time-exhausting, and is sometimes impossible for minerals with low symmetry. To reduce the involved difficulty, Dowty (1978) proposed that $Abs_{\text{total}}$ can be produced by polarized analyses along six vibration directions on any three orthogonal planes of a given sample, and subsequently Libowitzky and Rossman (1996) have theoretically and experimentally evaluated this approach.

Empirically, $Abs_{\text{total}}$ may be obtained from the thickness-normalized integrated absorbance along any three mutually perpendicular directions ($X'$, $Y'$ and $Z'$):

$$Abs_{\text{total}} = Abs_{X'} + Abs_{Y'} + Abs_{Z'}$$  \hspace{1cm} (4)

Johnson and Rossman (2003) have experimentally tested this approach using one anorthite sample (GRR 1968), and their measured $Abs_{\text{total}}$ agreed with that from the three principal axes to within 5% relative. A re-examination of that sample by a later work from the same group (Mosenfelder et al. 2015), however, argued that the method yielded overestimated $Abs_{\text{total}}$ by $>30\%$, which may have been caused by heterogeneity of H-species in the sample (Mosenfelder et al. 2015). In a recent report by Shuai and Yang (2017), the validity of Eq (4) has been carefully evaluated with a large number of well-characterized samples and also theoretical approach. The results show that Eq (4) works for samples even at extreme cases, where the absorption bands are both intense (e.g., samples up to ~4 mm thick) and strongly anisotropic, and has the same accuracy as Eq (3) for samples with a reasonable thickness (e.g., up to ~1 mm as what we commonly work with). The method of Eq (4) requires preparing the sample by double-polishing a crystal along any two perpendicular
planes only, without the necessity to orient it. This greatly simplifies the quantification of H-species in anisotropic minerals by polarized FTIR spectroscopy.

Still, however, there are circumstances where the sample crystals are too small to be prepared for polarized FTIR analyses along different directions. In this case, the frequently adopted alternative is the less demanding unpolarized measurements, which require the preparation of a double-polished section only and are commonly easy to achieve. Two approaches are available here. One is the frequency-dependent calibration of Paterson (1982), which is based on an empirical correlation between the OH stretching frequency and the molar absorption coefficient of quartz and silicate glass:

\[
c = \frac{X_i}{150 \cdot \gamma} \int \frac{A(\nu)}{3780 - \nu} d\nu
\]

where \(X_i\) is a density-dependent factor, \(\gamma\) is an orientation factor, and \(A(\nu)\) is the thickness-normalized absorbance for a given wavenumber \(\nu\) (e.g., for a unit thickness of 1 cm). This calibration (labeled as Method 1 in this study) was the first generic method specifically designed for determining the concentration of H in minerals and glasses. An apparent merit is that it does not require an externally determined calibration coefficient, and this makes it frequently employed. A critical assumption made for Method 1 is that both the absorption frequency and intensity of a unit amount of H are constants, which are unfortunately not correct for minerals (and glasses). It should also be pointed out that the \(\gamma\) of 1/3 was proposed by Paterson (1982) under the assumption that the orientation distribution of the OH groups is isotropic (see Table 1 in Paterson 1982), which is certainly
not the case for anisotropic minerals, and that the $\gamma$ was initially used to relate an
unpolarized measurement from a particular direction to $\text{Abs}_{\text{total}}$, different from the value of
1/3 proposed in later work which relates the average unpolarized absorbance on unoriented
grains to $\text{Abs}_{\text{total}}$ (Kovács et al. 2008; Withers 2013). The uncertainty of Method 1 was
usually assumed to be ~30-50%, although it has been argued that it might be much larger
(e.g., Libowitzky and Rossman 1996; Bell et al. 2003). The other approach can be viewed
as modified after Eqs (2) and (5), by combining the orientation factor and externally
determined calibration coefficients:
$$
\frac{c}{\text{unpol,avg Abs}} = \frac{1}{e \cdot \gamma}
$$
where $\text{Abs}_{\text{unpol,avg}}$ is the thickness-normalized integrated absorbance averaged over a large
number of randomly oriented crystals, and $\gamma$ is taken as 1/3. This calibration (labeled as
Method 2 in this study) has also been widely used (e.g., Katayama and Nakashima 2003;
Koga et al. 2003; Xia et al. 2006; Grant et al. 2007; Yang et al. 2008), although the
background had not been strictly established. Later, theoretical and empirical work has
been carried out, and an equation in the similar form (by replacing $\gamma$ with 1/3 directly) has
been deduced, which explains why a factor 1/3 is required (Kovács et al. 2008; Withers
2013). In principle, Method 2 works for samples where the absorption bands are less
intense or weakly anisotropic, e.g., the maximum linear absorbance is $<0.3$ or the ratio of
maximum and minimum absorbance is $\sim1$ (Kovács et al. 2008; Withers 2013). Also, it
requires measurements on a statistically meaningful number of randomly oriented grains
(e.g., 10 or even more), where caution must be taken for thin sections cut from untreated
samples directly since lattice-preferred orientations (LPO) are usually developed in natural
and synthetic materials (that is, the sample grains are actually not perfectly unoriented).
The uncertainty of Method 2 was usually assumed within ~20-30%. Sometimes, this
method has also been applied to samples with only a few grains (e.g., <5) or even for a
single grain (e.g., Koga et al. 2003), but the uncertainty has not been evaluated directly.

SAMPLES AND METHODS

Samples for the measurements are H-annealed and natural Ol, Cpx and Opx single crystals.
The annealed Ol samples are from our previous work (Yang et al. 2014b; Yang 2015, 2016;
Shuai and Yang 2017), and the annealed Cpx and Opx samples were from the present work,
following the method reported in our previous studies (Yang et al. 2014b; Yang 2015, 2016;
Shuai and Yang 2017). A summary of the samples is given in Table 1 and in the Appendix,
note that these samples are from three same starting crystals: Ol from Dak Lak (Vietnam),
Cpx from Asku (China), and Opx from Tanzania, of which the former two and crystals
from the same area as the latter one have been used in our H incorporation experiments
(Yang et al. 2014b, 2016; Yang 2015, 2016; Shuai and Yang 2017). In general, the crystals
are of gem-quality, although fractures were sometimes developed in the annealed crystals
due to stress-related compression and/or decompression during the H-annealing runs at
elevated conditions. For each sample, a single crystal was prepared by double-polishing
along two perpendicular planes, where polarized FTIR spectra were recorded along three
mutually perpendicular directions, following the method of Shuai and Yang (2017), and
unpolarized FTIR spectra were taken on the two perpendicular planes. On the other hand,
double-polished randomly oriented grains of the natural Cpx and Opx crystals, 10 grains for each, were prepared for unpolarized analyses. Thickness of the prepared samples is usually about 150-900 μm as measured by a Mitutoyo digital micrometer.

FTIR spectra were obtained with a Bruker Vertex 70V FTIR spectrometer coupled with a Hyperion 2000 microscope at the School of Earth Sciences and Engineering, Nanjing University. A total of 128 or 256 scans were accumulated for each spectrum with a globar source, a KBr/Ge beam-splitter, a mid-band MCT detector, an aperture of ~60×60 μm and a resolution of 4 cm$^{-1}$. A Zn-Se wire-grid polarizer was used for polarized radiation, and polarized spectra were measured with the electric field vector ($E$) parallel to three mutually perpendicular directions. Optically clean and inclusion- and crack-free areas were chosen for the analyses. During the measurements, the optics of the spectrometer were always kept under vacuum, and the optics of the microscope were continuously purged by purified, H$_2$O- and CO$_2$-free air. Baseline corrections of the spectra were carried out by performing a spline fit method defined by points outside the integrated region (Fig. 1). Several baseline corrections were conducted on representative spectra, and the variation of the integrated absorbance of each spectrum, i.e. the arbitrary uncertainty, is usually <10% (mostly <5%). This is normally the best what could be achieved in the community for processing the baseline corrections of any FTIR spectra, either polarized or unpolarized. The integral mineral-specific FTIR absorption coefficients of Bell et al. (1995) for Cpx and Opx and of Bell et al. (2003) for Ol were used for calibrating the H$_2$O contents. However, adoption of the coefficients does not affect the evaluation of the present study, and in particular, the test
of the accuracy of Method 2 is independent of the choice of coefficient (since the same
calibration coefficient is used for both polarized and unpolarized work).

RESULTS AND DISCUSSION

Profile FTIR analyses demonstrate no zoned patterns in the studied crystals (Fig. 2), as also
documented in our available reports (Yang et al. 2014b; Yang 2015, 2016). Representative
polarized and unpolarized FTIR spectra are shown in Figs. 3 and 4. H$_2$O contents of the
samples are given in Tables 1 and 2, and are plotted in Figs. 5 and 6. A summary of the
linear absorbance and H$_2$O contents of the samples are also given in the Appendix.

H-species in the samples

Significant absorption bands in the wavenumber range 3700-2800 cm$^{-1}$ are observed for all
the samples (Figs. 2-4). The bands centered at ~ 3610, 3597, 3573, 3566, 3543, 3524, 3510,
3483, 3448, 3407, 3392, 3353, 3325 and 3179 cm$^{-1}$ for the Ol samples, which are typical
for OH groups in many mantle-derived olivines (Matsyuk and Langer 2004; Demouchy et
al. 2006) and H-annealed Fe-bearing olivines (Demouchy and Mackwell 2006; Yang and
Keppler 2011; Yang 2012, 2015, 2016; Kovács et al. 2012; Yang et al. 2014b; Shuai and
Yang 2017; Demouchy et al. 2017). The bands centered at ~3646, 3600, 3558, 3528, 3460
and 3355 cm$^{-1}$ for the Cpx samples and at ~3685, 3600, 3544, 3514, 3415, 3370 and 3065
cm$^{-1}$ for the Opx samples, which are nearly the same as those reported for OH groups in
the corresponding minerals, either natural or H-annealed (e.g., Ingrin et al. 1989; Skogby et
al. 1990; Rauch and Keppler 2002; Stalder et al. 2015; Turner et al. 2015; Yang et al. 2016;
It should be noted, however, that the OH bands are actually different between the natural and H-annealed pyroxene samples, although their peak frequencies show some similarity (Figs. 3 and 4). For Cpx, the H-annealed samples demonstrate the most significant band at ~3646 cm$^{-1}$, with very weak bands at ~3600-3300 cm$^{-1}$, while the starting natural samples are characterized by intense bands at ~3600-3300 cm$^{-1}$, with relatively weak band at ~3646 cm$^{-1}$ (Figs 3b and 4a). For Opx, the H-annealed samples show the most profound bands at ~3600, 3415 and 3370 cm$^{-1}$, in obvious contrast to the starting natural samples where the most intense bands are observed at ~3513 and 3063 cm$^{-1}$; in particular, the sharp band at ~3600 cm$^{-1}$ of the H-annealed samples appears absent in the natural Opx, the sharp band at ~3513 cm$^{-1}$ of the natural Opx is greatly weakened in the H-annealed Opx, and the small band at ~3415 cm$^{-1}$ of the natural Opx is broadened and enhanced in the H-annealed Opx (Figs. 3c and 4b). Similar features have also been reported for Cpx and Opx (Rauch and Keppler 2002; Yang et al. 2016; Shuai and Yang 2017). Because the pyroxenes in this work are from the same starting materials and the chemistry of major- and minor-elements is broadly the same for either the Cpx or Opx samples, the observed differences between the qualitative and quantitative spectral characteristics of natural and H-annealed crystals may reflect different types and populations of defects involved in them. Very likely, the annealings at elevated conditions changed the defect population of the samples, which have in turn affected the incorporation of OH groups (Shuai and Yang, 2017).
Quantification of H-species with unpolarized analyses

The H$_2$O contents of the samples, by polarized analyses along three mutually perpendicular directions of each crystal, are ~25 to 420 ppm H$_2$O for Ol, 50 to 280 ppm H$_2$O for Cpx, and 30 to 170 ppm H$_2$O for Opx (Table 1). The contents of the H-annealed samples reprocessed in this study agree well with those produced in our available work (Yang et al. 2014b; Yang 2015, 2016; Shuai and Yang 2017), and the slight difference, commonly within 10% and mostly within 5% relative, is caused by the arbitrary uncertainty involved in the spectral baseline corrections by different operators. These values, representing the true H$_2$O contents of the samples by considering the “Background” Section above, are used to evaluate the quantification of OH groups with the two frequently adopted unpolarized analyses, namely the Method 1 and Method 2.

Method 1. The H$_2$O contents estimated by this approach, either obtained on a single grain (or on one of the two planes of each prepared crystal) or the average value of multi-grains (or of the two planes of each prepared crystal), differ clearly from those by polarized analyses (Fig. 3a, 3c and 3e). In general, the content determined by a single unpolarized analysis is apparently lower, and could be underestimated by a factor of up to ~6 for Ol, 3 for Cpx and 2 for Opx. The average content of unpolarized analyses on 2 or 10 randomly oriented grains (or planes) demonstrates smaller deviation from the true one, but is still lower by a factor of ~2.5-5.0 (on average 3.2) for Ol, 1.1-2.4 (on average 1.7) for Cpx and 1.2-1.4 (on average 1.3) for Opx (according to the data in Table 1). Broadly speaking, this method works better for Cpx and Opx than for Ol, and clearly a general upward revision is
needed for the estimated H$_2$O content. The observation that the H$_2$O content of Ol calibrated by this method is ~3 times lower is in excellent agreement with that of Bell et al. (2003), where the same conclusion has been reached for H$_2$O in natural olivines. This would mean that the method is actually inadequate for precise OH quantification. In case very rough information of sample H$_2$O content is required only or an externally determined calibration coefficient is not available for the target mineral, this method could be applied; however, the uncertainty could be up to ~80%, even when the average value of analyses on multi-grains is considered.

**Method 2.** The H$_2$O contents estimated by this approach, either obtained on a single grain (or on one of the two planes of each prepared crystal) or the average value of multi-grains (or of the two planes of each prepared crystal), also show a variable but generally low degree of deviation from those determined by polarized measurements (Fig. 3b, 3d and 3f). In general, the value by a single unpolarized analysis ranges from ~40% lower to 70% higher than the true content for all the studied samples and minerals, although the data mostly cluster around the 1:1 reference line. The average contents of unpolarized analyses on 2 or 10 randomly oriented grains (or planes) fall mostly within ±25% of the true ones, although the deviation can in some cases be ~40%. Therefore, the H$_2$O content in optically anisotropic minerals estimated by Method 2 is generally more accurate that that by Method 1. The accuracy of a single unpolarized analysis is relatively poor, as argued theoretically (Kovács et al. 2008; Withers 2013). The average contents from two unpolarized analyses on two different planes of the samples, in other words two grains of different orientations,
are usually acceptable given an accuracy level of ±25%. However, it does not mean that unpolarized measurements on two randomly-chosen unoriented grains of a given sample could always yield a similar accuracy in H$_2$O content, because the two planes in this study are not arbitrary but mutually perpendicular (meaning that the orientations of the OH vectors are spatially relevant) which could affect the measured spectra and thus the H$_2$O content. This is actually obvious from our measured data on the natural cpx and opx, where the content of a single unpolarized analysis could be ~60% higher or 40% lower than the true value (Fig. 5d and 5f) and the average of two analyses on two grains could deviate by ~40-60% in the extreme cases. For both the natural cpx and opx samples, the average H$_2$O contents from unpolarized analyses on 10 unoriented grains of random orientations are essentially the same as those determined by polarized measurements, consistent with each other within ~7% (Fig. 5 and Table 2).

In summary, Method 2 has apparent advantage over Method 1 in the context of accuracy in the quantification, as the uncertainty could be ~25% or smaller even only two unpolarized measurements from two unoriented grains are considered. For a given sample, the relative variation of H$_2$O contents estimated by a single unpolarized analysis is usually larger for cpx and opx than for oli (demonstrated by both Method 1 and Method 2: Fig. 5), which could be reasonably accounted for by the more anisotropic absorption bands in the former than in the latter (Figs. 3 and 4 and Appendix). However, it appears clear that the average value produced by Method 2 is acceptable mostly with an accuracy within ±25% (Fig. 5d and 5f), even for samples whose absorption bands are both strong and strongly anisotropic.
A regression processing of all the data demonstrates that the average contents by Method 2 are globally in excellent agreement with the true values by polarized work (Fig. 6). Thus, it would be usually fine to apply Method 2 to both natural and synthetic samples where the information of H$_2$O contents is to be determined. In some studies, a particularly high level of accuracy is required for quantifying the H content, e.g., for documenting the quantitative effect of OH on some physical properties of the host minerals such as ionic diffusivity and electrical conductivity. Concerning these studies, the application of Method 2 may yield H$_2$O contents of acceptable accuracy (within ±25%) even only from two unpolarized measurements on two unoriented grains, but it may cause large uncertainty to H-related physical parameters because the uncertainty is non-systematic, in that it could underestimate but could also overestimate the contents (Figs. 5 and 6). For example, electrical conductivity is sensitive to OH in nominally anhydrous minerals, and the large variation of the experimentally determined OH-related exponential factor, $r$ in the Arrhenius equation which is linked to the nature of the charged H and ranges from ~0.6 to 1.5 in available reports (e.g., Huang et al. 2005; Yang et al. 2011, 2012; Yang 2012; and references therein), is very likely caused by the non-systematic error in characterizing the H$_2$O contents of the involved samples (Yang et al. 2012; Li et al., 2017).

Finally, the experimental test demonstrates that Method 2 works even for samples whose bands are both intense and strongly anisotropic (Fig. 5 and Appendix). This, in fact, differs from the theory in available reports that the method works in principle for samples with
either less anisotropic bands or the maximum linear intensity is relatively small (i.e. <0.3: Kovács et al. 2008; Withers 2013). In particular, Withers (2013) has shown by numerical simulation that, for unpolarized measurements on randomly oriented grains with a number of up to 10, the yielded average values always underestimate the H$_2$O content, although the convergence toward the true content is apparent with increasing the number of studied grains (see Fig. 5 in that paper). This is not supported by our experimental work where the average values of unpolarized analyses on randomly oriented grains, 2-10 for each sample, could either overestimate or underestimate the contents (i.e. non-systematic patterns: Fig. 5b, 5d and 5f). The difference might be caused by some assumptions or approximations made in the theoretical deductions of previous work, concerning for example the complex relationship between spectral absorbance and transmittance and the simplification in the mathematical processing including the numerical integration of some complex equations (see more details in: Kovács et al. 2008; Withers 2013). This means that the requirements for applying Method 2 is actually not that strict as those established theoretically (Kovács et al. 2008; Withers 2013), and the data of this work may provide a basis for reevaluating the theoretical background in early work. Further studies on the theoretical background of Kovács et al. (2008) and Withers (2013) would reconcile the difference between theoretical and experimental approaches.

IMPLICATIONS

By carrying out a careful experimental work on a series of H-bearing Ol, Cpx and Opx with both polarized and unpolarized measurements, the results of this study provide by far
the first systematic evaluation for quantifying H-species in anisotropic minerals by unpolarized infrared spectroscopy. Our data demonstrate clearly that the H$_2$O content estimated by a single unpolarized analysis could be inaccurate if the polarized absorbance indicatrix is highly anisotropic, and the uncertainty could be up to $\sim$80% in extreme cases. Moreover, unpolarized Method 1 commonly underestimate the H$_2$O content by a factor of up to $\sim$6, even when the average of multi-grain measurements is taken into account, and unpolarized Method 2 is in general more precise, with an accuracy mostly within $\pm$25%. Method 1 could be employed to estimate the H$_2$O content of samples when externally determined mineral-specific calibration coefficients are not available, but the very large uncertainty must be considered. Method 2 could be applied safely to samples where only rough information is required for the amount of H-species, but particular caution must be paid to the random orientation of the involved grains because of the development of LPO in natural and synthesized samples. For example, unpolarized analyses on 10-20 or even more unoriented grains in a rock section with strong LPO of the studied mineral may be physically equivalent to work on only one or just a few grains.

Accepting the uncertainties, unpolarized FTIR determinations could be used to quantify the amount of H in optically anisotropic minerals. This can be readily conducted, because the required procedure of sample preparation is pretty simple (when compared to polarized work). Our results provide a solid basis for evaluating the accuracy of the yielded data and for future studies on measuring H$_2$O contents in anisotropic minerals and on a quantitative understanding of the effect of water on physical properties of the host minerals. In case the
mineral grains in a sample section are randomly oriented, analyses of 10 grains by Method 2 could yield H$_2$O contents of nearly the same accuracy as the polarized measurements, but the prerequisite might not be easily reached for simply-prepared sample sections (e.g., the grains are not perfectly randomly oriented). It should be further noted that the protocols for calculating water contents are actually different between Method 1 and Method 2 (See the Background Section). Therefore, the contents of H-species estimated by Method 1 can only be recalculated to Method 2 if the original spectra are provided, and a simple conversion of the concentrations by a simple factor would introduce large non-systematic uncertainty. At last, we would like to emphasize that, for very precise work, polarized FTIR analyses along the three principal axes (the standard approach) or along any three random but orthogonal directions (the modified method: Shuai and Yang (2017)) should be considered first if the samples allow the preparation (e.g., with a suitable grain size).

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**FIGURE CAPTIONS**

**Fig. 1** Representative spectra of olivine (a), clinopyroxene (b) and orthopyroxene (c) for baseline correction. Uncorrected, baseline and corrected spectra are shown from top to bottom by black, blue and red lines, respectively. The spectra were normalized to 1 cm thickness and vertically offset.

**Fig. 2** Representative profile FTIR spectra of H-species in olivine (a), clinopyroxene (b) and orthopyroxene (c). Numbers above each spectrum show the integrated absorbance (cm$^{-2}$, with an uncertainty of <10%, mostly <5%, due to baseline correction) and the estimated distance from crystal center (μm in parentheses). The spectra were normalized to 1 cm thickness and vertically offset.

**Fig. 3** Representative polarized and unpolarized FTIR spectra of H-species in H-annealed olivine (a), clinopyroxene (b) and orthopyroxene (c). The bottom polarized spectra were taken along three random but orthogonal directions, and the top unpolarized spectra were taken over two perpendicular planes. Conditions for the H-annealing of the samples are shown in the figures. The spectra were normalized to 1 cm thickness and vertically offset.

**Fig. 4** Polarized and unpolarized FTIR spectra of H-species in natural clinopyroxene (a) and orthopyroxene (b). The bottom polarized spectra were taken along three random but orthogonal directions, and the top unpolarized spectra were taken on 10 randomly oriented grains. The spectra were normalized to 1 cm thickness and vertically offset.

**Fig. 5** Plots of H$_2$O contents determined by polarized measurements and by unpolarized
Method 1 (a) and unpolarized Method 2 (b). Data points were taken from Tables 1 and 2. Open symbol represents a single unpolarized analysis, and solid symbol represents the average value of multi-grain analyses (purple, by averaging 2 unpolarized spectra from 2 perpendicular planes of a crystal; red, by averaging 10 unpolarized spectra from 10 randomly oriented grains). Dashed lines are for reference only. Error bars were assumed 10% relative (note that the uncertainty of our data was usually <10% and mostly <5% relative: see text).

**Fig. 6** Plot of H$_2$O contents by polarized analyses and by unpolarized Method 2. The average contents of Tables 1 and 2, shown also in Fig. 5, are plotted together for a global linear regression. The fitting was forced to pass through the zero point, and the yielded slope is 1.02±0.03 ($r^2=0.95$). Error bars were assumed 10% relative (note that the uncertainty of our data was usually <10% and mostly <5% relative: see text).
### Table 1  Summary of olivine, clinopyroxene and orthopyroxene samples and H\textsubscript{2}O contents

<table>
<thead>
<tr>
<th>No. (\text{a})</th>
<th>ppm H\textsubscript{2}O (polarized)(\text{b})</th>
<th>ppm H\textsubscript{2}O (unpolarized, Method 1)(\text{c})</th>
<th>ppm H\textsubscript{2}O (unpolarized, Method 2)(\text{d})</th>
<th>summary of samples(\text{e})</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(reported) (reprocessed) (plane 1) (plane 2) (mean)</td>
<td>(plane 1) (plane 2) (mean)</td>
<td>(plane 1) (plane 2) (mean)</td>
<td>(P) (GPa)</td>
</tr>
<tr>
<td>oli(PC11)</td>
<td>240 237 68 91 79.5 230 310 270 3.5</td>
<td>1100 NNO</td>
<td>Yang et al. (2014b)</td>
<td></td>
</tr>
<tr>
<td>oli(1)</td>
<td>90 97 29 30 29.5 82 86 84 1</td>
<td>1100 IW</td>
<td>Yang (2015)</td>
<td></td>
</tr>
<tr>
<td>oli(4)</td>
<td>43 38 16 16 16 32 67 49 1</td>
<td>1100 IW</td>
<td>Yang (2015)</td>
<td></td>
</tr>
<tr>
<td>oli(6)</td>
<td>195 184 100 37 68.5 248 155 201 3</td>
<td>1100 IW</td>
<td>Yang (2015)</td>
<td></td>
</tr>
<tr>
<td>oli(15)</td>
<td>175 165 46 76 61 153 231 192 3</td>
<td>1100 IW</td>
<td>Yang (2015)</td>
<td></td>
</tr>
<tr>
<td>oli(5)</td>
<td>200 212 77 51 64 233 173 203 3</td>
<td>1100 IW</td>
<td>Yang (2015)</td>
<td></td>
</tr>
<tr>
<td>oli(11)</td>
<td>200 190 64 52 58 191 130 161 2.5</td>
<td>1100 NNO</td>
<td>Yang (2016)</td>
<td></td>
</tr>
<tr>
<td>oli(12)</td>
<td>254 262 55 56 55.5 233 217 225 2.5</td>
<td>1100 HM</td>
<td>Yang (2016)</td>
<td></td>
</tr>
<tr>
<td>oli(9)</td>
<td>138 127 26 25 25.5 88 74 81 1.5</td>
<td>1300 NNO</td>
<td>Yang (2016)</td>
<td></td>
</tr>
<tr>
<td>oli(18)</td>
<td>400 422 175 157 166 561 454 508 5</td>
<td>1100 NNO</td>
<td>Yang (2016)</td>
<td></td>
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<tr>
<td>oli(oli-0)</td>
<td>436 423 133 154 143.5 404 449 426 7</td>
<td>1100 NNO</td>
<td>Shuai and Yang (2017)</td>
<td></td>
</tr>
<tr>
<td>oli(oli-1)</td>
<td>23 26 9 7 8 33 30 31 1</td>
<td>900 NNO</td>
<td>Shuai and Yang (2017)</td>
<td></td>
</tr>
<tr>
<td>oli(oli-3)</td>
<td>70 75 28 23 25.5 94 76 85 2.5</td>
<td>1200 NNO</td>
<td>Shuai and Yang (2017)</td>
<td></td>
</tr>
<tr>
<td>oli(oli-6)</td>
<td>61 66 12 44 28 58 58 58 1</td>
<td>1100 NNO</td>
<td>Shuai and Yang (2017)</td>
<td></td>
</tr>
<tr>
<td>cpx(natural)</td>
<td>48 19 20 20 38 41 39 -</td>
<td>-</td>
<td>this study</td>
<td></td>
</tr>
<tr>
<td>cpx(A67)</td>
<td>279 140 207 174 235 278 257 3</td>
<td>1100 IW</td>
<td>this study</td>
<td></td>
</tr>
<tr>
<td>cpx(A69)</td>
<td>146 156 103 129 186 148 167 2</td>
<td>1100 HM</td>
<td>this study</td>
<td></td>
</tr>
<tr>
<td>opx(natural)</td>
<td>31 25 21 23 36 29 33 -</td>
<td>-</td>
<td>this study</td>
<td></td>
</tr>
<tr>
<td>opx(A85)</td>
<td>173 104 144 124 119 141 130 2</td>
<td>1100 IW</td>
<td>this study</td>
<td></td>
</tr>
<tr>
<td>opx(A60)</td>
<td>65 69 38 54 88 47 67 1</td>
<td>1000 NNO</td>
<td>this study</td>
<td></td>
</tr>
</tbody>
</table>

\(\text{a}\) Labels in the parentheses are the sample as used in the referred literatures.

\(\text{b}\) Values labeled as ‘reported’ are taken from the referred literatures directly, and values labeled as ‘reprocessed’ are the recalculated data from

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the re-measured FTIR spectra of this study. The slight differences are caused by the arbitrary uncertainty due to performing baseline
corrections by different operators, but are generally within 10% relatively (mostly <5%). All the data are calculated from three polarized FTIR
spectra along three mutually perpendicular directions of each sample crystal (see text for more details). oli samples are from the same starting
crystal from Dak Lak, Vietnam, cpx samples are from the same starting crystal from Asku, China, and opx samples are from the same starting
crystal from Tanzania (see text for details).

c Values for the spectra taken along two perpendicular planes by the unpolarized Method 1 and the average data (see text for details).
d Values for the spectra taken along two perpendicular planes by the unpolarized Method 2 and the average data (see text for details).
d Abbreviations of \( O_2 \) buffers: NNO, Ni-NiO; IW, Fe-FeO; HM, Fe\(_2\)O\(_3\)-Fe\(_3\)O\(_4\).

Uncertainty of H\(_2\)O contents is usually <10% relative (see text).
Table 2  H$_2$O contents of clinopyroxene and orthopyroxene samples by unpolarized analyses on 10 randomly oriented grains

<table>
<thead>
<tr>
<th>No.</th>
<th>ppm H$_2$O$^a$ (randomly oriented grains)</th>
<th>(mean)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cpx(natural)</td>
<td>48$^*$</td>
<td>48$^*$</td>
</tr>
<tr>
<td>unpolarizd, Method 1</td>
<td>14 24 21 29 36 22 34 22 25</td>
<td>26</td>
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<tr>
<td>unpolarizd, Method 2</td>
<td>28 50 47 58 75 36 76 72 30 35</td>
<td>51</td>
</tr>
<tr>
<td>Opx(natural)</td>
<td>31$^*$</td>
<td>31$^*$</td>
</tr>
<tr>
<td>unpolarizd, Method 1</td>
<td>23 25 21 21 15 18 21 21 26</td>
<td>21</td>
</tr>
<tr>
<td>unpolarizd, Method 2</td>
<td>34 34 30 29 18 24 27 26 33 41</td>
<td>30</td>
</tr>
</tbody>
</table>

$^a$ Values for the unpolarized spectra taken from randomly oriented grains and the average data.

$^*$ H$_2$O contents by polarized analyses are shown for reference (the values are also given in Table 1).

Uncertainty of H$_2$O contents is usually <10% relative (see text).
Fig. 1
Fig. 2
Fig. 3
Fig. 4
Open symbols, single grain; Solid symbols, mean value

**Fig. 5**
Fig. 6