Reviews in Mineralogy & Geochemistry
Vol. 62, pp. 155-167, 2006
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Water in Natural Mantle Minerals I: Pyroxenes

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INTRODUCTION

A large number of studies of water in pyroxenes have confirmed that essentially all pyroxenes of terrestrial origin as a rule contain substantial amounts of OH, varying as a function of chemical composition and geological occurrence. The highest OH-concentrations are observed in mantle-derived samples, and it is now well established that both clino- and orthopyroxene can be considered as major host minerals for water in the mantle (e.g., Bell and Rossman 1992; Bell et al. 2004; Bolfan-Casanova 2005).

The first firm observations of OH in pyroxenes were made more than three decades ago. Even earlier, the "excess" water recorded in many wet-chemical analyses of pyroxenes and other nominally anhydrous minerals had been taken as indications of structurally bonded water, although it was difficult to confirm whether this "excess" water was really due to intrinsic OH, or if it was caused by fluid or solid inclusions, or contaminants on cracks and surfaces. A water incorporation model based on OH ions replacing O at their normal structural positions in pyroxenes was proposed by Martin and Donnay (1972), who also suggested that OH-containing nominally anhydrous minerals could provide the main storage mechanism for water in the mantle. Somewhat later Wilkins and Sabine (1973) published IR spectra of several nominally anhydrous minerals, including a diopside from crustal occurrence (Fig. 1). The spectra contained sharp OH absorption bands which were verified by deuterium exchange, and the water contents were also analyzed by an electrolytic technique, which showed considerably lower concentrations than what had earlier been indicated from wet-chemical analyses. Also Runciman et al. (1973) observed absorption bands in the OH range in a spectroscopic study in the full infrared to UV-range of an enstatite from Kimberley, South Africa, which they suspected to be caused by traces of OH. A more detailed study based on polarized IR spectra

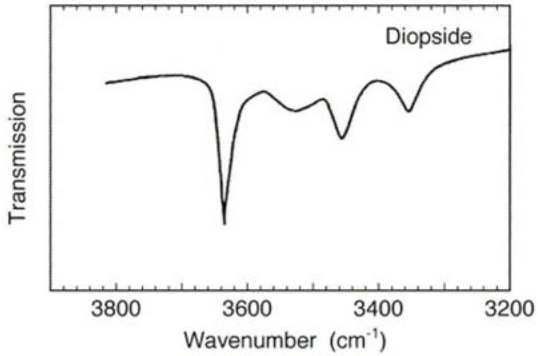


Figure 1. IR transmission spectrum of diopside from Rotenkopf, Tyrol. Modified after Wilkins and Sabine (1973).

1529-6466/06/0062-0007$05.00 DOI: 10.2138/rmg.2006.62.7

of diopside was published by Beran (1976), who presented an incorporation model based on crystal-chemical arguments and the pleochroic behavior of the absorption bands. The study was followed up by an investigation of additional pyroxenes (Beran 1981), some of which were of high-pressure origin. An incorporation model for OH also in enstatite was presented by Beran and Zemann (1986) based on polarized IR spectroscopy.

Later studies addressed the stability relations of OH in the pyroxene structures by experimental methods; Ingrin et al. (1989) and Skogby and Rossman (1989) showed that hydrogen could be diffused out from the structure at elevated temperatures, but also restored under reducing conditions, with a thermal stability in the same order as OH in amphiboles and micas. The generality of the occurrence of OH in pyroxenes was surveyed by Skogby et al. (1990). The study comprised over 50 samples from various types of geological environments, and showed that OH occurs in terrestrial pyroxenes as a rule, with the highest concentrations recorded in samples from mantle origin.

Much of the more recent interest has been focused on samples of mantle origin, due to the perspectives of pyroxenes forming a mantle reservoir for water, together with other NAMs (nominally anhydrous minerals), and the imposed effects on mantle properties (e.g., Smyth et al. 1991; Bell and Rossman 1992; Rossman 1996; Peslier et al. 2002; Bell et al. 2004; Koch-Müller et al. 2004). However, also crustal pyroxenes have been considered in some studies, (e.g., Johnson et al. 2002), as well as pyroxenes occurring in subducted crustal rocks (e.g., Katayama et al. 2003, 2005).

OH ABSORPTION BANDS IN IR SPECTRA

The vast majority of studies of water species in mantle pyroxenes have been performed using FTIR spectroscopy. Apart from estimates of water concentration, IR spectra provide valuable information regarding the local OH dipole environment, as orientation and possible O-H··O distances (cf. Libowitzky and Beran 2006). The different types of OH bands observed in IR spectra of pyroxenes are discussed in the following section. As the OH bands in samples from mantle and crustal origin are similar, both types of occurrences are considered. A more thorough overview of the occurrence of water in crustal pyroxenes is given in Johnson (2006).

Diopside

Infra-red spectra of diopside normally contain four major OH absorption bands, which show two types of pleochroic behavior (Fig. 2). One band occurs around 3640 cm^{-1} and is strong in the α and β directions, but weak or absent in the γ direction. Three bands occurring close to 3535, 3460 and 3355 cm^{-1} have a different pleochroism with γ as the strongest direction, and weaker absorption parallel α and β. The band at 3355 cm^{-1} is sometimes absent in mantle diopside (Peslier et al. 2002). The pleochroic schemes observed for different pyroxene minerals are summarized in Table 1.

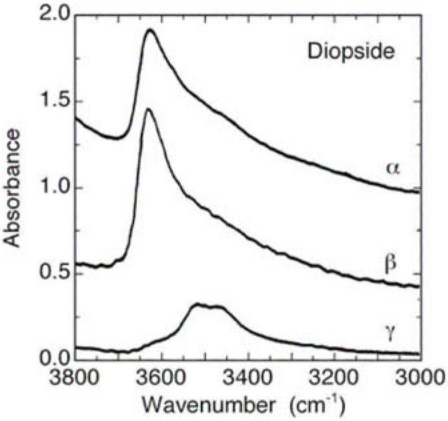


Figure 2. Polarized IR spectra of diopside from a basalt megacryst, Maui, Hawaii, normalized to 1 mm thickness. Sample no. 7 from Skogby et al. (1990).

Augite

Augite spectra are normally rather similar to diopside spectra, with one band

Table 1. Pleochroism of OH bands in clino- and orthopyroxene spectra.

Mineral	Wavenumber (cm^{-1})			
	3630 - 3640	**3530 - 3540**	**3460**	**3355**
Diopside	$\alpha = \beta, \gamma = 0$	$\gamma > \alpha = \beta$	$\gamma > \alpha = \beta$	$\gamma > \alpha = \beta$ *
Augite	$\alpha = \beta, \gamma = 0$	$\gamma > \alpha = \beta$	$\gamma > \alpha = \beta$	—
Omphacite	$\alpha = \beta, \gamma = 0$ *	$\gamma > \alpha = \beta$	$\gamma > \alpha = \beta$	—
	3600 - 3610	**3410 - 3560**	**3060 - 3300**	
Orthopyroxene	$\alpha = \beta, \gamma = 0$ *	$\gamma > \alpha \approx \beta$	$\gamma > \alpha > \beta$	

* Band not always observed.

close to 3630 cm^{-1} polarized in the α and β directions, and two bands close to 3530 and 3460 with the pleochroism $\gamma > \alpha = \beta$ (Fig. 3). Compared to diopside, the 3355 cm^{-1} band is absent, and the bands are normally somewhat broader and slightly shifted to lower wavenumbers.

Omphacite

IR spectra of omphacite are similar to those of augite, with one α– and β–polarized band around 3630 cm^{-1} and two bands around 3530 and 3460 cm^{-1} with their strongest absorption in the γ direction (Fig. 4). However, omphacite spectra differ from augite spectra in that the 3460 cm^{-1} band in omphacite is normally much stronger than the other bands, and that the 3630 cm^{-1} bands is sometimes absent (Koch-Müller et al. 2004; Katayama et al. 2005).

Orthopyroxene

OH absorption bands in orthopyroxene spectra are quite different compared to those in clinopyroxene spectra, and show also substantial variation. One group of bands occurs at 3600-3610 cm^{-1} and is polarized in the α and β directions (e.g., Bell et al. 1995; Rauch and Keppler 2002), but is not always present in orthopyroxene spectra (Skogby et al. 1990). A second group of bands with the pleochroic behavior $\gamma > \alpha \approx \beta$ occur at 3560, 3510 and 3410 cm^{-1} (Fig. 5). A third group occur at the relatively low wavenumbers 3300, 3210 and 3060 cm^{-1}, with the pleochroic scheme $\gamma > \alpha > \beta$ (e.g., Bell et al. 1995; Peslier et al. 2002).

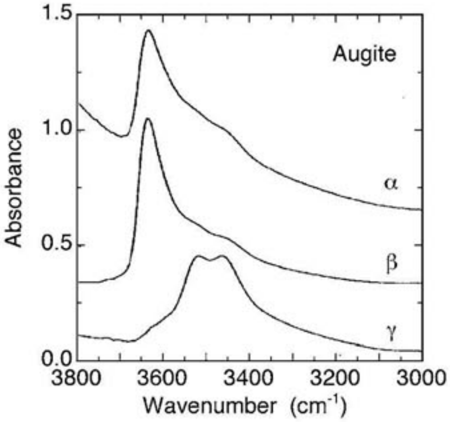


Figure 3. Polarized IR spectra of augite from mantle diatreme xenolith, Hopi Butte, Arizona, normalized to 1 mm thickness. Modified after Skogby et al. (1990).

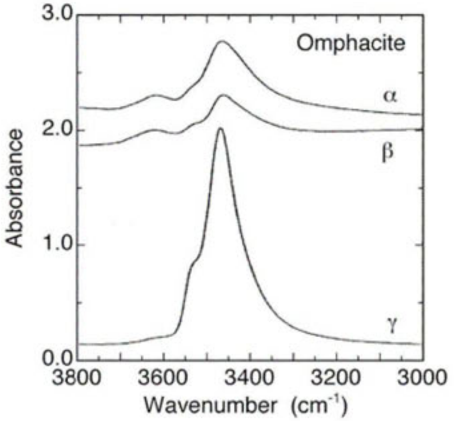


Figure 4. Polarized IR spectra of omphacite from an eclogite xenolith in kimberlite, Roberts Victor Mine, South Africa, normalized to 1 mm thickness. Modified after Skogby et al. (1990).

The OH bands in orthopyroxene spectra are often sharper than those observed in clinopyroxene spectra, except the bands in the third group that follow the general trend with increasing band width towards lower wavenumbers.

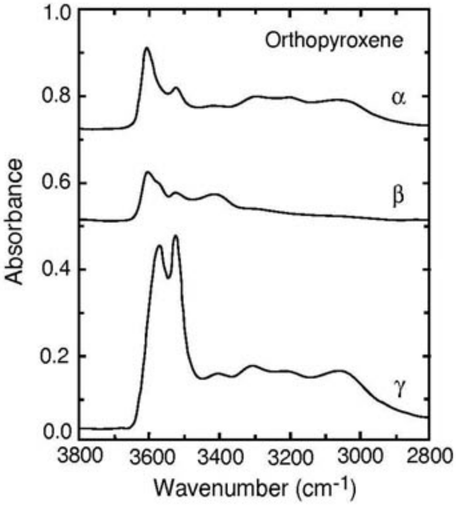


Figure 5. Polarized IR spectra of orthopyroxene from a spinel-peridotite xenolith, Simcoe, WA, normalized to 1 mm thickness. Modified after Peslier et al. (2002).

Absorption from inclusions

Besides normal "pyroxene" OH bands, absorption features from hydrous phases included in the pyroxene structures are sometimes encountered. Absorption bands caused by fluid and glass inclusions are considerably broader than pyroxene bands, and can normally be distinguished from them by the H_2O bending (1630 cm^{-1}) and combination (5200 cm^{-1}) modes, and their isotropic behavior in polarized measurements. However, they may cause severe distortions of the spectral baseline that make quantification procedures more problematic.

Amphibole lamellae frequently occur in pyroxenes, as documented by HRTEM studies (e.g., Veblen and Buseck 1981; Ingrin et al. 1989). Amphiboles normally have sharp and well-defined OH absorption bands, which are sometimes observed in pyroxene spectra. As they occur at somewhat higher frequencies, they can normally be easily distinguished in pyroxene spectra (Fig. 6.). Amphibole bands appear to be more frequent in spectra of crustal pyroxenes than mantle pyroxenes. Since the molar absorption coefficients of amphibole OH bands are very high (Skogby and Rossman 1991), IR spectroscopy provides a very efficient means to detect low amounts (ppm level) of submicroscopic amphibole lamellae in pyroxenes (Skogby et al. 1990; Andrut et al 2003).

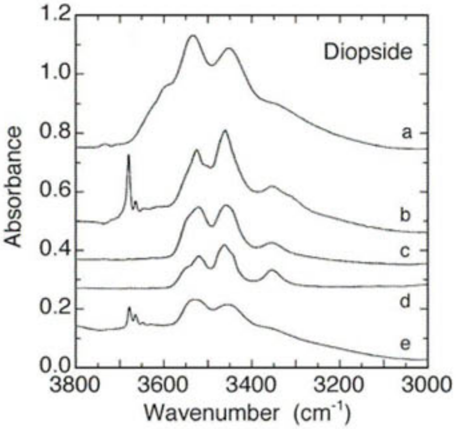


Figure 6. IR spectra for diopside crystals in γ-polarization normalized to 1 mm thickness. Sample occurrence: a) xenolith in mantle diatreme, Hopi Butte, AZ; b) metamorphic, Outokumpu, Finland; c) metamorphic, Binntal Vallis, Switzerland; d) metamorphic, Mount Bity, Madagascar; e) metamorphic, Sinnidal, Norway. Note sharp bands around 3670 cm^{-1} that are due to amphibole inclusions. Modified after Skogby et al. (1990).

Also sheet silicates have been shown to occur in mantle pyroxenes and cause absorption in the OH range. In a study based on FTIR spectroscopy and HRTEM characterization, Koch-Müller et al. (2004) identified nm-sized inclusions of clinochlore, amesite and biotite in omphacite samples. They interpreted unusually strong absorption bands observed at 3600-3624 cm^{-1} to be caused by these hydrous sheet silicate inclusions (Fig. 7). Similar strong absorption bands were observed by Katayama and Nakashima (2003) in spectra of clinopyroxene from an eclogite.

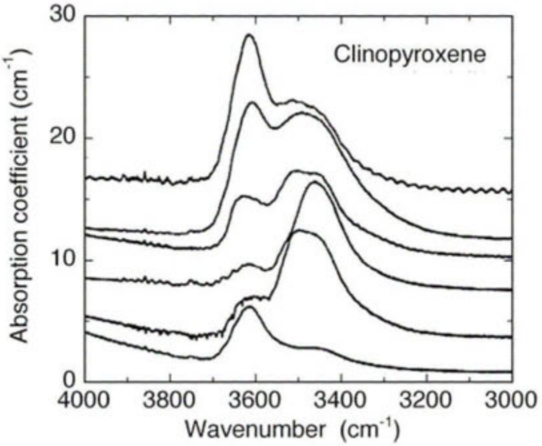


Figure 7. Polarized IR spectra of omphacite and omphacitic clinopyroxene from eclogite and granulite occurrences in Yakutia, Russia. Bands around 3600-3625 cm^{-1} are related to hydrous nano-inclusions. Spectra are polarized along α and normalized to 1 cm thickness. Modified after Koch-Müller et al. (2004).

The relatively weak α- and β-polarized absorption bands normally observed in this region in omphacite spectra (Table 1) have been interpreted to be due to intrinsic OH groups. However, the possibility that also these bands are due to sheet silicate inclusions can at present not be ruled out, and there is hence a strong need for further studies to investigate how widespread these nanoscale inclusions are in omphacitic pyroxenes.

CORRELATIONS OF OH AND SAMPLE CHEMISTRY

The incorporation of hydrogen in the pyroxene structure needs to be accompanied by other substitutions, or formation of vacancies, to maintain charge-balance. Such coupled hydrogen incorporation mechanisms are expected to lead to correlations between OH concentrations and sample chemistry. Several studies have searched for such correlations (Skogby et al. 1990; Peslier et al. 2002; Bell et al. 2004; Koch-Müller et al. 2004), taking both trace, minor and major elements into account. However, well-defined correlations have only rarely been found. As the amounts of OH are relatively high in mantle derived pyroxenes with concentrations ranging from hundreds up to a few thousands wt-ppm H_2O, trace elements are generally not present in sufficient amounts to account for the hydrogen incorporation mechanisms. Minor elements (e.g., Al, Cr, Fe^{3+}, Na) and vacancies are more likely candidates, and have also been shown to be at least weakly correlated with OH concentration or absorbance of individual bands in IR spectra.

For clinopyroxenes, Skogby et al. (1990) observed a correlation between absorption coefficients of the high-wavenumber (3640 cm^{-1}) bands in spectra of diopside and augite samples and the amount of trivalent ions (Fig. 8). Positive correlations of OH absorbance and Al contents in a suite of clinopyroxene were also found by Peslier et al. (2002), but in this case with the absorption band at 3540 cm^{-1} (Fig. 9). Furthermore, Andrut et al. (2003) noted a correlation of OH and Al in a zoned gem-quality diopside crystal of metamorphic origin. Aluminum appears to be involved also in hydrogen incorporation in omphacite, as shown by Koch-Müller et al. (2004) who observed a correlation between aluminum in the tetrahedral position and the absorbance of bands in the 3500-3540 cm^{-1} region (Fig. 10a). In addition, they noted a continuous shift of the position of the main absorption band in this region with the amount of tetrahedrally coordinated Al (Fig. 10b). Other elements that have shown to be correlated with OH concentration include Ti and K, as reported by Bell et al. (2004) in a study of megacrysts from the Monastery kimberlite. They found that H and Ti were correlated with an atomic ratio of 1:1 (Fig. 11), but concluded that this does not necessarily mean that a 1:1 substitutional

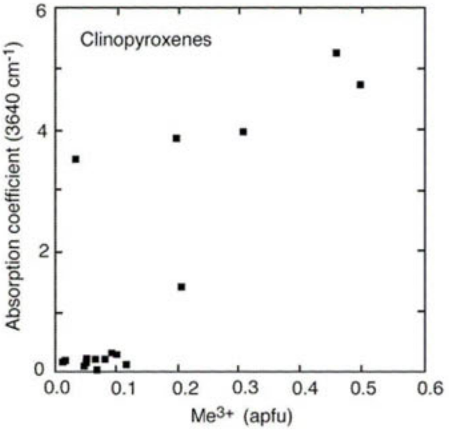
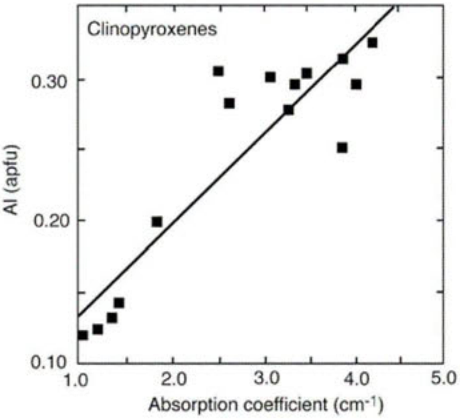


Figure 8. Summed absorption coefficients for OH bands around 3640 cm^{-1} plotted versus Al + Cr + Fe^{3+}, in atoms per formula unit. Data represent diopside-hedenbergite, augite and aegirine-augite samples of crustal and mantle origin. Data from Skogby et al. (1990).

Figure 9. Correlation between absorption coefficients for the 3540 cm^{-1} band in clinopyroxene spectra and Al content. Data obtained on spinel-peridotite xenolith samples from Mexico and Simcoe, WA. Data from Peslier et al. (2002).



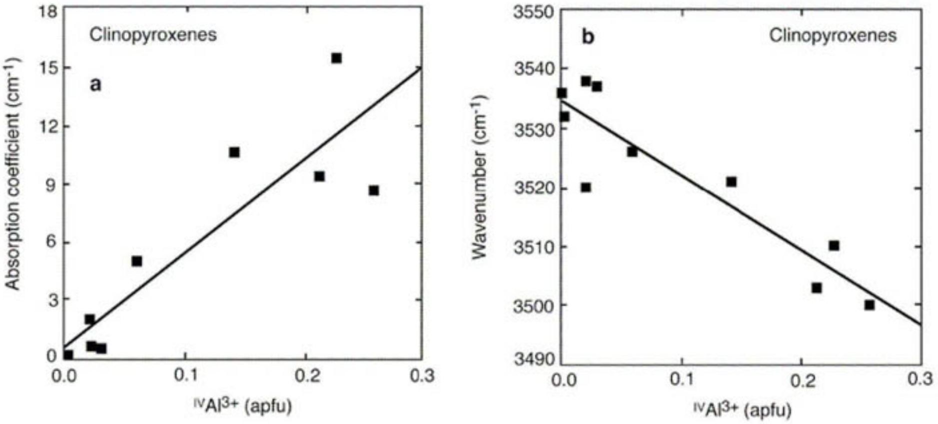


Figure 10. Plots of (a) linear absorbance for γ-polarized OH bands at 3500-3540 cm^{-1} in omphacitic clinopyroxene, and (b) main wavenumber, versus tetrahedrally coordinated Al (apfu). Samples from eclogite and granulite occurrences in Yakutia, Russia. Modified after Koch-Müller et al. (2004).

mechanism can be inferred, as also other elements (e.g., K) were found to be correlated with H, but at strongly different atomic ratios.

In general, the correlations of OH concentration and sample chemistry that have been observed in natural samples have been relatively weak. An explanation for the absence of stronger correlations can be that the variable degrees of OH saturation caused by equilibration in different geological environments may obscure possible correlations, when samples from different geological environments are considered. A possible way to decrease the effect of various degrees of OH saturation is to search for correlations between ratios of OH band intensities and sample chemistry. Using this approach, Skogby et al. (1990) observed a pronounced correlation between the ratio of the intensities of high- and low-wavenumber bands in clinopyroxene spectra and the ratio of the concentration of trivalent ions and Fe^{2+} (Fig. 12).

Apart from correlations with minor elements, hydrogen concentrations have also been shown to follow trends with major elements. This is exemplified by the studies of Peslier et al. (2002), which displayed negative correlations with the major elements Si, Mg and Ca, and Bell et al. (2004), which showed that OH concentrations follow differentiation trends coupled to Ca-number (Ca/[Ca+Mg] ratio) for clinopyroxenes from the Monastery kimberlite.

For omphacite, and also sodic clinopyroxenes, several studies have shown that OH absorbances correlate with the amount of cation vacancies at the *M*2 site. This was first observed by Smyth et al. (1991) who studied a suite of sodic clinopyroxenes from South African mantle eclogites. The presence of vacancies at the *M*2 site in mantle eclogite has been confirmed by crystal-chemical methods (McCormick 1986), and can be seen as a Ca-Eskola ($Ca_{0.5}\square_{0.5}AlSi_2O_6$) component. The solubility of the Ca-Eskola component in clinopyroxenes under *P* and *T* conditions representative for eclogite facies has been verified experimentally (Gasparik 1986). Smyth et al. (1991) found that the intensity of the band near 3460 cm^{-1} correlates with the amount of *M*2 cation vacancies, and that samples with high Ca-Eskola components contained the highest OH concentrations observed in pyrox-

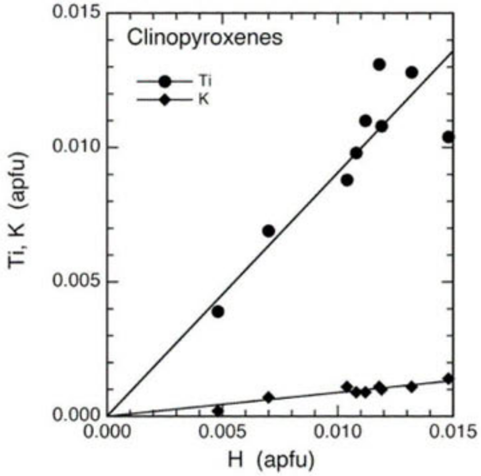


Figure 11. Correlation of H with (a) Ti, and (b) K, in clinopyroxene from mantle-derived megacrysts from the Monastery kimberlite, South Africa. Modified after Bell et al. (2004).

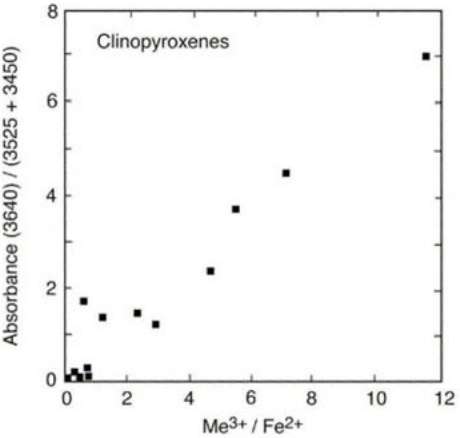


Figure 12. Ratio of summed absorbances for OH bands at 3640 and 3450-3525 cm^{-1} plotted vs. the atomic ratio (Al + Cr + Fe^{3+})/Fe^{2+}. Data represent diopside-hedenbergite, augite and aegirine-augite samples of crustal and mantle origin with Fe > 0.10 apfu. Data from Skogby et al. (1990).

enes. Similar relations with pronounced correlations of bands in the 3460 cm^{-1} area and cation vacancies (Fig. 13) have also been found for other series of mantle eclogite clinopyroxenes (Koch-Müller et al. 2004), as well as crustal eclogite clinopyroxenes (Katayama et al. 2003, 2005). Moreover, experimental studies (Bromiley and Keppler 2004) have demonstrated that small amounts of Ca-Eskola components considerably increase the amount of OH incorporation in synthetic jadeite.

Some of the studied clinopyroxenes characterized by relatively high Ca-Eskola components also contain exsolved garnet and kyanite, indicating that the precursor pyroxene phase has contained even higher amounts of *M*2 vacancies. By extrapolation of the observed trends between OH absorbance and vacancies, OH concentrations ranging up to several thousands ppm H_2O have been estimated (Smyth et al. 1991).

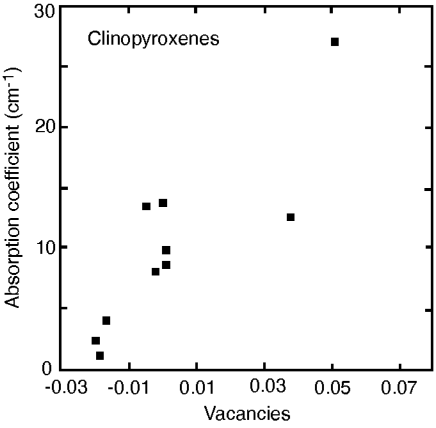


Figure 13. Plot of linear absorbance for γ-polarized OH bands at 3500-3540 cm^{-1} in omphacitic clinopyroxene as a function of vacancy concentration, calculated as 4 minus total cations per 6 oxygen atoms. Samples from eclogite and granulite occurrences in Yakutia, Russia. Data from Koch-Müller et al. (2004).

Mantle orthopyroxenes generally show less chemical variability than mantle clinopyroxenes, and correlations between OH absorbances and compositions have been observed only in a few cases. However, in the study of Monastery kimberlite samples, Bell et al. (2004) found OH concentrations to follow a trend of decreasing OH with Fe enrichment, and also Al following closely the same trend. A weak positive correlation of Al and OH in mantle orthopyroxene was also observed by Peslier et al. (2002), as well as for OH and whole-rock Al contents. These positive correlations observed for OH and Al in mantle orthopyroxene is further supported by work on synthetic orthopyroxene (Rauch and Keppler 2002; Stalder 2004) which have shown that the OH solubility increases strongly with Al content, and that the bands in the higher wavenumber range (>3400 cm^{-1}) are caused by OH associated with Al.

WATER CONCENTRATION IN MANTLE PYROXENES

Ortho-and clinopyroxenes have been shown to carry the largest amounts of water among the major upper mantle minerals, and it is evident that pyroxenes play important roles both in providing a repository for water in the upper mantle and in mantle water recycling processes. A fairly large number of studies have addressed the specific amounts of OH in pyroxenes from different mantle occurrences, including kimberlites (e.g., Bell et al. 1992, 2004), peridotites of different types (e.g., Skogby et al. 1990; Peslier et al. 2002) as well as eclogites from both mantle and crustal environments (Smyth et al. 1991; Katayama and Nakashima 2003; Koch-Müller at al. 2004; Katayama et al. 2005). Most studies have relied on IR spectroscopy for quantification of water concentrations. The calculation procedures involved to translate spectral absorption parameters to absolute water concentration data require calibration by independent water analysis methods, which have continuously been improved over time. An overview of suitable hydrogen analysis methods and their application in calibrations of OH absorbances in IR spectra is given in Rossman (2006). As also the IR measurements can be performed in different ways, for instance concerning polarization, background subtraction, and use of linear or integrated intensities, published concentration data are not always directly comparable. A summary of published data on contents in mantle pyroxenes are given in Table 2, including information on analytical procedures.

The OH concentrations vary as a function of mineral species and composition, and in some cases also in relation to the type of mantle environment. However, strong variations are also observed for samples within each mineral group from similar environments. Calcic clinopyroxenes (diopside and augite) from peridotites vary in concentration from 140 to 740 ppm H_2O, whereas orthopyroxene show lower concentrations in the range 40 to 530 ppm H_2O. In general, orthopyroxenes hold about half the amount of OH being present in co-existing clinopyroxenes. The calcic clinopyroxenes do not appear to show significant correlation with type of the environment in general. However, Demouchy (2004) observed an increasing trend in water concentrations in diopside when going from spinel lherzolite via garnet/spinel lherzolite to garnet lherzolite. Similarly, Bell et al. (1992) observed the highest OH concentration for orthopyroxene in coarse-grained samples from garnet peridotites, but noted that these samples may have been affected by metasomatic reactions in the mantle.

The highest levels of water concentrations among pyroxenes have been recorded for omphacite and sodic clinopyroxene (Smyth et al. 1991; Katayama and Nakashima 2003; Koch-Müller at al. 2004; Katayama et al. 2005). Reported concentrations (Table 2) range

Table 2. Summary of observed OH concentrations in mantle pyroxenes.

Geological occurrence	Mineral	# of samples	OH conc. (wt-ppm H_2O)	Analysis method*	Ref.
kimberlite and alkali basalt xenoliths, mantle eclogite	calcic cpx	5	200 - 530	1	[1]
	omphacite	1	640		
	opx	3	60 – 260		
mantle eclogite	omphacite	11	130 - 970	1	[2]
kimberlite and alkali basalt xenoliths, mantle eclogite	calcic cpx	7	150 – 590	2	[3]
	omphacite	2	470 - 1080		
	opx	10	50 – 460		
basalt xenoliths	cpx	3	388 – 492	2	[4]
	opx	3	174 – 212		
spinel peridotite xenoliths	cpx	15	140 – 528	3	[5]
	opx	16	39 – 265		
crustal eclogite	omphacite	6	230 - 870	4	[6][7]
kimberlite megacrysts	cpx	9	195 – 620	2	[8]
	opx	3	215 – 263		
peridotite xenoliths	diopside	4	150 - 420	5	[9]
	opx	5	70 - 310		
mantle and crustal eclogite	cpx	8	31 – 514	6	[10]
			61 - 872	2	

* ***Analysis based on***: 1) IR, based on a linear molar absorption coefficient ε_{OH} = 150 L/(mol·cm), Skogby et al. (1990); 2) IR, calibrations of Bell et al. 1995, with integral molar absorption coefficients I_{cpx}= 38300, I_{opx}= 80600 L/(mol·cm^2); 3) IR, calibrations of Bell et al. 1995, using "specific" integral absorption coefficients I'_{cpx}= 7.09, I'_{opx}= 14.84 ppm^{-1}cm^{-2}); 4) SIMS data, unpolarized IR data using calibration of Bell et al. 1995 (see above) indicate that the OH concentrations are twice as high as those listed here; 5) Unpolarized IR data, based on the calibration of Paterson (1982), with the general integral molar absorption coefficient defined as $I_H = 150·(3780 – \nu)$; 6) IR, calibration of Libowitzky and Rossman (1997), with the general integral molar absorption coefficient defined as $I_{H2O} = 246.6·(3753 – \nu)$.

References: [1] Skogby et al. (1990); [2] Smyth et al. (1991); [3] Bell et al. (1992); [4] Ingrin and Beran (2001); [5] Peslier et al. (2002); [6] Katayama and Nakashima (2003); [7] Katayama et al. (2005); [8] Bell et al. (2004); [9] Demouchy (2004); [10] Koch-Müller et al. (2004)

from 30 to 1080 ppm $H_2$0, although it should be noted that a mineral specific IR calibration for omphacite is lacking, and the reported concentrations based on IR data should be viewed with some caution. This is exemplified by recent SIMS data on omphacite from a crustal eclogite occurrence (Katayama et al. 2005) that indicated that the concentration based on IR absorbances was overestimated by a factor of two. Additional uncertainties regarding the high water concentrations observed in omphacite are the observations of nano-inclusions of hydrous phases related to high-wavenumber bands observed by Koch-Müller et al. (2004). A strong dependence of water concentration and crystallization depth was observed by Katayama et al. 2005 (Fig. 14), who related the pressure-dependence to increased stability of the Ca-Eskola component. However, Koch-Müller et al. (2004) observed a reversed situation with unusually low concentrations (31 ppm) in diamond-bearing eclogite xenoliths and the highest concentrations (437-514 ppm) in lower-pressure grospydites and granulites. They interpreted the unusually low water concentrations for the samples from the high-pressure occurrence as being caused by low water activity during crystallization, or alternatively by hydrogen loss during uplift.

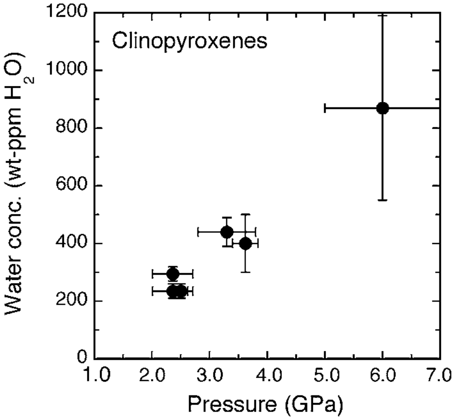


Figure 14. Pressure dependence of water contents in omphacite in eclogites from the Kokchetav massif, Kazachstan. Data from Katayama et al. (2005).

IMPLICATIONS FOR WATER IN THE UPPER MANTLE

A fundamental question regarding OH contents in mantle pyroxenes, as well as in other mantle-derived NAMs, is whether the water concentrations recorded in xenolith samples are representative for the conditions in the upper mantle, or if the original hydrogen contents have been reset during different types of ascent processes. The substantial amounts of kinetic data for hydrogen diffusion in pyroxenes that now are available (e.g., Hercule and Ingrin 1999; Carpenter Woods et al. 2000; Stalder and Skogby 2003; Ingrin and Blanchard 2006) indicate that major resetting is indeed possible, also during relatively fast ascent processes (Ingrin and Skogby 2000). On the other hand, several lines of evidence indicate that OH concentrations representative for mantle conditions to large extents are preserved in pyroxenes and other mantle NAMs.

A major argument for preservation of mantle OH concentrations comes from the observations of systematic correlations between sample chemistry and OH content. In a study of OH concentration of pyroxenes from spinel peridotites from the sub-arc mantle wedge, Peslier et al. (2002) found that the OH contents were correlated with sample composition, but also with the chemistry of associated spinels and whole-rock xenolith data. These parameters can be expected to be completely independent of xenolith transport processes, which indicate that the OH contents were neither reset to large extents.

An important parameter for OH incorporation in peridotite pyroxenes appears to be the redox conditions. This was demonstrated in the study by Peslier et al. (2002) who observed a clear negative correlation between OH concentration and oxygen fugacities estimated from spinel compositions in a series of samples collected from different regions of the sub-arc mantle wedge, which is known to be more oxidized than other parts of the upper mantle. The low OH concentrations observed in the more oxidized environments were interpreted to be caused by redox dehydration reactions associated with metasomatism and partial melting, which led to a loss of more than half of the initial pyroxene water contents. Estimates of the water budget in subduction zones indicated, however, that the water released from NAMs in the sub-arc mantle wedge only account for a minor proportion of ca 5% of the total water in this environment. Negative correlations between oxygen fugacity and OH in pyroxene have also been observed in experimental studies (e.g., Skogby 1994).

Support for preservation of mantle OH concentrations in pyroxenes is put forward by the study of Bell et al. (2004) on different NAMs from a suite of megacrysts from the Monastery kimberlite. They observed that the OH contents in both clino- and orthopyroxenes followed trends with other elements in Fe-enrichment and Ca content, reflecting igneous differentiation. In accordance with the study of Peslier et al. (2002), they concluded that such systematic behavior would unlikely be observed if OH contents were fully reset at crustal environments at later stages of ascent processes. Furthermore, they noted that the relatively high OH concentrations recorded for the Monastery olivines (54-262 ppm H_2O) according to experimental studies require equilibration pressures corresponding to mantle conditions, and are not compatible to resetting in crustal environments.

Even if arguments exist for preservation of original mantle water contents in pyroxenes found in xenoliths, the available kinetic data regarding dehydrogenation reactions (cf. Ingrin and Blanchard 2006) indicate that hydrogen loss may be significant. The fastest reaction in this respect involves concomitant oxidation of Fe^{2+} according to the redox reaction:

$$Fe^{2+} + OH^{-} = Fe^{3+} + O^{2-} + \tfrac{1}{2}\,H_2$$

This reaction has been shown to be considerable faster than dehydrogenation reactions involving more rigorous structural changes (e.g., cation diffusion, resetting of defect chemistry). Significant dehydrogenation following this reaction will lead to enhanced Fe^{3+}/Fe^{2+} ratios, similar to what have been observed for some mantle-derived amphiboles (e.g., Dyar et al. 1992). The ferric iron contents of mantle pyroxenes can hence be used to estimate the maximum amounts of hydrogen that may have been lost via the redox reaction. By adopting this approach, Ingrin and Skogby (2000) found that the ferric iron levels observed in mantle pyroxenes correspond to a maximum loss of 900 ppm H_2O for clinopyroxene and 570 ppm H_2O for orthopyroxene.

Apart from providing a host phase for mineral-bound water in the upper mantle, pyroxenes appear to play an important role for water recycling related to subduction zones. The high OH concentrations recorded in omphacitic pyroxenes from both crustal and mantle occurrences indicate that they provide an efficient means for water transport down to the deeper levels of the upper mantle, beyond the stability fields of the hydrous minerals. In a recent study, Katayama et al. (2005) showed that the water contents of omphacite from the Kokchetav massif, which has been subducted to a depth of 180 km, contain up to 870 ppm H_2O and that water contents systematically increase with pressure (Fig. 14). They suggested that omphacite, together with garnet and rutile, in subducted crust may carry water down towards the transition zone at depths around 400 km, where the eclogite minerals are expected to transform to majoritic garnet and stishovite.

ACKNOWLEDGMENTS

E. Libowitzky, A. Beran and H. Keppler are thanked for providing constructive reviews of this manuscript.

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