

Synchrotron infrared spectroscopy of OH-chondrodite and OH-clinohumite at high pressure

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ABSTRACT

High-pressure synchrotron infrared (IR) absorption spectra were collected at ambient temperature for OH-chondrodite and OH-clinohumite up to 38 and 29 GPa, respectively, using argon as the pressure-transmitting medium. The crystal structures of both clinohumite and chondrodite are preserved up to the maximum pressure. However, disordering of the silicate framework appears to become more pronounced at high pressure based on significant broadening of the IR bands with increasing pressure. All three OH bands in both structures shift linearly to higher frequency with pressure up to 18 GPa. Above 18 GPa, the variation of OH frequency with pressure remains linear; however, the slopes for the three OH bands are significantly different as a result of different degrees of hydrogen bonding. The IR results are compared to those from recent Raman studies in which water was used as the pressure-transmitting medium.

INTRODUCTION

Structural differences between orthosilicate humites and olivine can be defined in terms of two substitutions: $4\text{O} \leftrightarrow (\text{F,OH})$ and $\text{Si} \leftrightarrow \square$ (vacancy), which are expressed by the formula $\text{M}_2\text{Si}_{y-1}\text{O}_{4y-4}(\text{F,OH})_4$, where $y = 3, 5, 7, 9$ for norbergite, chondrodite, humite and clinohumite, respectively (Ribbe 1980). In view of their close structural similarity, it is not surprising that the water content of some hydrated olivines is due to the presence of humite-like monolayers intergrown with olivine on a sub-microscopic scale (Kitamura et al. 1987; Risold et al. 2001). This suggests that the hydrogen atom environment in humites can provide useful insights into the local environment of OH defects in olivine. Humites may also be important phases involved in the storage, transport, and recycling of water in the mantle. Recent experimental work on the $\text{MgO-SiO}_2\text{-H}_2\text{O}$ system suggests that clinohumite could transport water into the transition zone (400 km) (Stalder and Ulmer 2001). A number of recent studies have discussed the significance of structurally bound water with respect to the rheological properties of the mantle (Hirth and Kohlstedt 1996; Williams and Hemley 2001).

The behavior of hydrous phases under mantle conditions is intimately linked to the nature of the hydrogen bond. For example, changes in the hydrogen bonding at pressure can affect both the compressibility and stability of hydrous minerals, such as lawsonite [$\text{CaAl}_2\text{Si}_2\text{O}_7(\text{OH})_2\cdot\text{H}_2\text{O}$] (Boffa Ballaran and Angel 2003; Pawley and Allan 2001; Daniel et al. 2000; Scott and Williams 1999) and brucite [$\text{Mg}(\text{OH})_2$] (Shinoda et al. 2002; Duffy et al. 1995a, 1995b; Catti et al. 1995; Parise et al. 1994).

In the absence of crystallographic data, the strengthening or weakening of hydrogen bonds is usually estimated based on the frequency shifts in OH-stretching modes. Negative shifts, i.e., a decrease in the OH vibrational frequency with pressure, imply a strengthening of hydrogen bonds at high pressure. By analogy, positive shifts are associated with a weakening of the

hydrogen bond. Note that the same effect would be observed if the O-H bond is compressed in structures where hydrogen bonding is very weak or absent. However, additional evidence from either experiment or theory is required to support this idea. In most hydrous phases, the strength of hydrogen bonds increases with pressure as $\text{O}\cdots\text{O}$ distances shorten.

In the case of humites, all OH bands in OH-clinohumite and OH-chondrodite shift to higher frequencies with pressure, based on Raman spectroscopic studies to ~40 GPa (Lin et al. 1999, 2000). The OH-clinohumite spectra also revealed a mode softening of one of the OH bands at ~13 GPa, which could be related to variations in the hydrogen bonding at pressure. This band splits into two bands at ~18 GPa. One of these bands shows positive pressure dependence whereas the other displays a negative dependence. Both positive and negative pressure dependencies have been observed for the OH vibrations in an IR study of an F-bearing chondrodite (Williams 1992). In contrast, a Raman study of an F-bearing chondrodite of similar composition showed only positive OH shifts, which were attributed to a lengthening of hydrogen bonds at pressure (Lin et al. 1999). However, this conclusion is not consistent with a recent high-pressure neutron powder study of F-bearing chondrodite (Friedrich et al. 2002). Interpretation of the spectroscopic data is difficult because: (1) the pressure dependence of the hydrogen-atom positions in the OH end-members has not been determined; and (2) humites are characterized by disordered hydrogen bond systems (Fig. 1). In OH-clinohumite and OH-chondrodite, the hydrogen atoms (H1 and H2) are statistically disordered over two sites (50% occupancy). Hydrogen bond distances range from 2.01 to 2.58 Å in OH-clinohumite and from 1.968 to 2.489 Å in OH-chondrodite (Berry and James 2001; Lager et al. 2001). The shortest hydrogen bond is formed between H1 and the pair of centrosymmetric O atoms, i.e., O9 in clinohumite or O5 in chondrodite. This bond is nearly straight with an O-H \cdots O angle of ~170°. Because the hydrogen atoms are located within cavities (Fig. 1),

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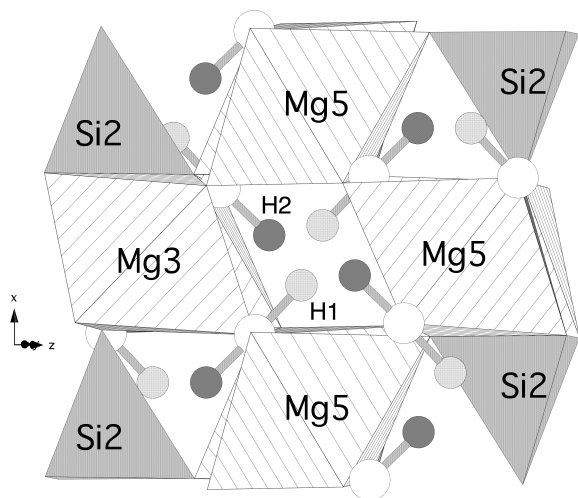


FIGURE 1. A portion of the OH-clinohumite structure showing the orientation of the O-H vectors within the cavities. The two H1 sites are related by a center of symmetry and cannot be occupied simultaneously (50% occupation). When one of the H1 sites is occupied, the H2 atom is bonded to the adjacent O9 atom, i.e., the O-H vectors point in the same direction.

the O-H vector is not highly constrained and can rotate in response to an increase in pressure (Friedrich et al. 2002).

In this study, IR spectra of polycrystalline samples of OH-clinohumite and OH-chondrodite were collected at ambient temperature to pressures of 38 and 29 GPa, respectively. The objectives of these experiments were to (1) confirm the positive pressure shifts observed in the Raman study using a pressure transmitting medium that remains quasi-hydrostatic up to the maximum pressure measured in this work; (2) re-examine the mode softening of the OH band in OH-clinohumite at ~13 GPa and the splitting of this band at ~18 GPa; (3) interpret the shifts in the OH bands in light of recent neutron powder diffraction data on OH-chondrodite and OH-clinohumite at ambient pressure and F-bearing chondrodite at high pressure; and (4) provide a basis for a more detailed study of these phases using single-crystal polarized infrared methods.

EXPERIMENTAL METHODS

OH-clinohumite and OH-chondrodite single crystals were synthesized at 7 GPa and 1000 °C and 3 GPa and 910 °C, respectively, in a 1000 ton Walker multi-anvil device at Haskell Laboratory, University College, London (Ross and Crichton 2001).

For the high-pressure IR absorption experiments, a symmetrical type diamond anvil cell (Mao et al. 1998) with type II diamond anvils was used for IR absorption measurements. To avoid any saturated absorption, a small amount of sample was placed on the center of one diamond anvil and the cell was carefully closed without any gasket. This created a thin pellet with thickness less than 1 μm and ~50 μm in diameter. A stainless gasket with a 150 μm hole was placed between the two anvils and several ruby grains were loaded into the gasket hole for pressure calibration. Argon gas was liquefied with liquid nitrogen and loaded into the sample chamber as a pressure-transmitting medium.

In situ high-pressure FTIR spectra were recorded from 4000 to 550 cm^{-1} on a Bruker IFS 66s/V FTIR spectrometer at the U2A beam line of National Synchrotron Light Source at Brookhaven National Laboratory. The spectrometer was equipped with a modified IRscope II infrared microscope, a KBr beam splitter, and an MCT detector adapted to the IR synchrotron source. To take the advantage of the high brightness of the synchrotron source, the aperture was set

to $20 \times 20 \mu\text{m}$ to ensure that only spectra of the sample or pure argon were obtained, respectively. In this case, both sample absorption and background/reference can be measured at the same pressure. All sample and reference spectra were collected with a resolution of 4 cm^{-1} and 1024 scans. The entire optical path was purged with dry nitrogen gas during the measurements to eliminate vapor absorption. The details of the synchrotron IR optical system are published elsewhere (Liu et al. 2001).

RESULTS AND DISCUSSION

Infrared spectra at ambient pressure

Figure 2 shows typical synchrotron IR absorption spectra of OH-clinohumite and OH-chondrodite at ambient conditions. The dominant IR absorption regions were found in the frequency ranges of 600–1100 and 3650–3500 cm^{-1} . Three distinct IR bands at 3526, 3561, and 3608 cm^{-1} observed in clinohumite and 3525, 3563, and 3607 cm^{-1} in chondrodite are related to OH-stretching vibrational modes. The slightly higher OH-stretching mode vibrational frequencies of clinohumite relative to chondrodite is consistent with the weaker hydrogen bonding observed in the clinohumite structure (see above). In the lower frequency region, on the other hand, the spectra of clinohumite and chondrodite are very similar except for two bands at 959 and 983 cm^{-1} for clinohumite vs. the single band at 992 cm^{-1} for chondrodite. It should be noted that relative intensities of the bands can change significantly in different experiments if there is a high degree of preferred orientation. All IR bands with frequencies at 800–1000 cm^{-1} are assigned to symmetric and asymmetric stretching modes of the silicate tetrahedron, SiO_4 , and the two bands below 800 cm^{-1} may be attributed to tetrahedral Mg translational modes (Cynn et al. 1996). The numbers of observed IR-active modes and Raman-active modes (Lin et al. 1999, 2000) are significantly smaller than those predicted from factor group analysis for both clinohumite and chondrodite. As noted by Lin et al. (1999, 2000) this may be partially due to preferred orientation and polarization effects. For the IR absorption spectra studied here, no bands below 600 cm^{-1} were observed because of the limit of the MCT detector. The IR bands at 800–1000 cm^{-1} are highly overlapped. Many modes may be degenerate or near degenerate.

Pressure dependence of IR absorption bands

Representative IR absorption spectra of clinohumite and chondrodite at several pressures and room temperature are shown in Figure 3. Under compression, all OH-stretching bands monotonically shift to higher frequencies similar to those observed in Raman studies (Lin et al. 1999, 2000). There is no significant change in band shapes in the pressure range studied here, although amplitudes of all IR bands decrease with increasing pressure due to band broadening at high pressure. This broadening is not the result of non-hydrostatic conditions because argon was used as the pressure medium. The changes that occur in the silicate region of the spectrum are very similar to those observed for the OH-stretching region, i.e., positive frequency shift, relative intensity change, and band broadening with increasing pressure. The difference between the bands at 983 and 959 cm^{-1} in clinohumite increases with pressure and the shoulder around 860 cm^{-1} is well resolved at high pressure in clinohumite as well as in chondrodite. On this basis, we conclude that the crystal structure of both clinohumite

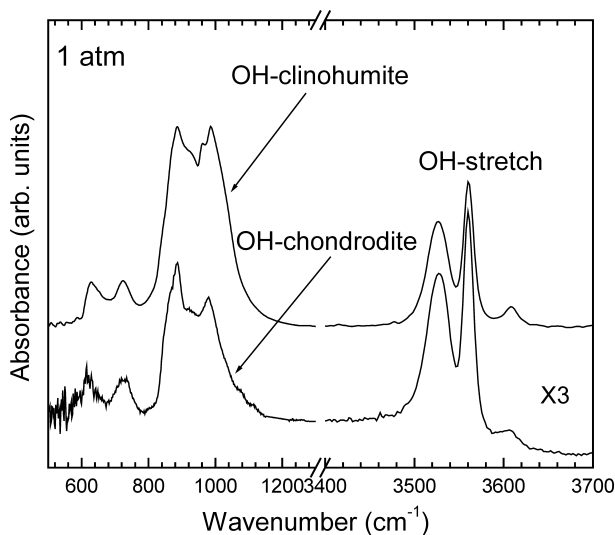


FIGURE 2. Synchrotron IR absorption spectra of OH-clinohumite and OH-chondrodite at ambient conditions.

and chondrodite is preserved up to the maximum pressures studied here. However, disordering of the silicate framework may become more pronounced, as indicated by the significant broadening of the IR bands with increasing pressure.

The pressure dependences of the IR frequencies of clinohumite and chondrodite are shown in Figure 4. The solid lines represent least-squares fits to the data (Table 1). All bands in the silicate region shift monotonically with pressure except for the band around 730 cm^{-1} in OH-chondrodite, which has a small pressure dependence (Fig. 4a). The pressure dependence of corresponding bands in the clinohumite and chondrodite spectra is very similar in the measured pressure range. Therefore, the response of the silicate framework to compression is comparable for both phases. Similar frequency shifts with pressure are also found in the OH-stretching region (Fig. 4b). However, our results differ from those reported in the Raman study (Lin et al. 2000). Neither the mode softening of the OH band at 3526 cm^{-1} in OH-clinohumite at $\sim 13\text{ GPa}$ nor the splitting of this band at $\sim 18\text{ GPa}$ were observed in the IR experiments. Instead, we found that all three OH bands shift linearly to higher frequency with pressure up to 18 GPa . Above 18 GPa to the maximum pressure, the variation in frequency remains linear but the slopes for the three bands are significantly different due most likely to different degrees of hydrogen bonding. The main difference between our work and the Raman studies is the use of argon rather than water as the pressure-transmitting medium. Argon offers the advantages that it is inert chemically and maintains a more quasi-hydrostatic sample environment than water.

The positive shift of OH-stretching modes in humites is notable. Positive pressure shifts measured in high-pressure IR and Raman spectra of F-bearing/OH-chondrodite (Williams 1992; Lin et al. 1999), OH-clinohumite (Lin et al. 2000), and hydrous magnesium silicates (Cynn and Hofmeister 1994; Hofmeister et al. 1999) have been attributed to H-H repulsions, lengthening of hydrogen bonds, weakening of the hydrogen bond due to changes in the O-H \cdots O angles, and O-H bond compression. In the case of humites, the first hypothesis is based

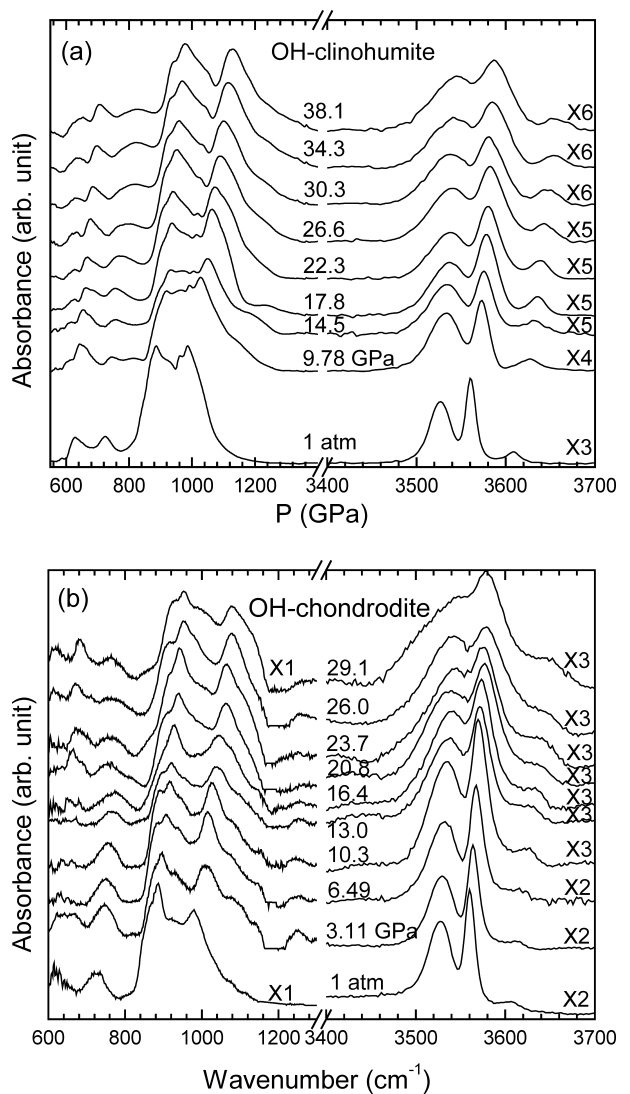


FIGURE 3. Infrared absorption spectra of OH-clinohumite (a) and OH-chondrodite (b) at ambient temperature and several different pressures.

on an incorrect interpretation of the crystallographic data (Lager et al. 2001). Short H-H distances (and strong H-H repulsions) are an artifact of the average structure determined by diffraction methods. At the local level, hydrogen atoms are never in close proximity. The second and third hypotheses are not consistent with recent neutron data for F-bearing chondrodite (Friedrich et al. 2002). Although a rotation of the O-H vector could lengthen the O \cdots H bond, possible changes in this bond length can be compensated for by compression of the O \cdots O distance. For example, in F-bearing chondrodite, the combined effect of rotation (O-D) and compression (O \cdots O) produces a slight decrease in the D \cdots F bond length and no significant change in the length of the D \cdots O bond. Finally, as noted previously, more evidence is needed to support the claim that the O-H bond shortens at high pressure even when the hydrogen bonding is very weak or absent. As a follow up to this study, single-crystal polarized IR measurements at pressure will be carried out using oriented sections of the F-bearing

TABLE 1. Observed vibrational modes and their frequency shifts with pressure in OH-clinohumite and OH-chondrodite

Samples	OH-clinohumite			OH-chondrodite		
	ν_0 (cm ⁻¹)	$b \times 10$ (cm ⁻¹ /GPa)	$c \times 10^2$ (cm ⁻¹ /GPa ²)	ν_0 (cm ⁻¹)	$b \times 10$ (cm ⁻¹ /GPa)	$c \times 10^2$ (cm ⁻¹ /GPa ²)
614	30.3	-1.4		628	9.9	3.4
720	22.4	1.7		737	28.4	-7.4
861	26.2	-1.6		860	30.2	-3.2
884	32.8	-2.5		887	28.3	-1.8
917	40.8	-4.2		922	26.1	-0.1
959	32.5 (0–18 GPa)			992	38.8	-2.6
983	51.0	-3.6				
3525.7	7.4 (0–18 GPa)			3527.2	6.7 (0–18 GPa)	
3560.7	10.9 (0–18 GPa)			3562.0	7.4 (0–18 GPa)	
3607.3	16.0 (0–18 GPa)			3606.7	14.1 (0–18 GPa)	

Note: A discontinuity in mode shifts is observed for all OH-stretching modes and one SiO₄ stretching mode at 960 cm⁻¹ in OH-clinohumite at ~18 GPa.

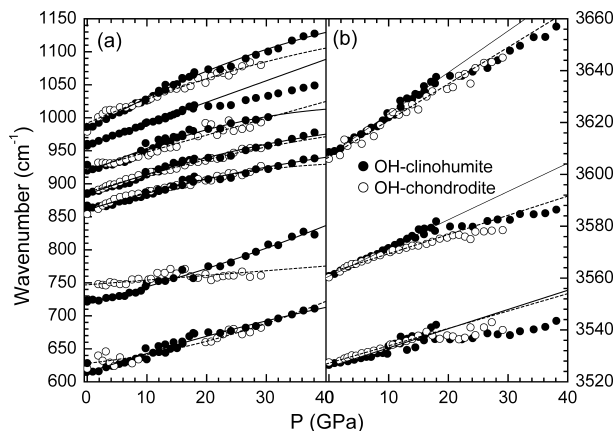


FIGURE 4. Pressure dependences of the IR band frequencies of OH-clinohumite (a) and OH-chondrodite (b) at ambient temperature. All data obtained under quasi-hydrostatic conditions with argon as a pressure-transmitting medium.

ing chondrodite investigated by Friedrich et al. (2002). The pressure dependence of the orientation of the O-H dipoles in the axial directions may provide more insights into the origin of the frequency shifts.

ACKNOWLEDGMENTS

We thank H.K. Mao for help and NSF-EAR-0073734 (GAL) and DOE (NSLS) for financial support. We thank Annette K. Kleppe for a thorough and constructive review of the manuscript.

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MANUSCRIPT RECEIVED OCTOBER 15, 2002

MANUSCRIPT ACCEPTED APRIL 14, 2003

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