High-pressure phase transitions and hydrogen incorporation into MgSiO₃ enstatite

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ABSTRACT

Hydrogen incorporation into orthoenstatite (Pbca), low-clinoenstatite (P2₁/c), and high-pressure clinoenstatite (C2/c) has been investigated using polarized and unpolarized infrared spectroscopy. Using shifts in OH stretching frequencies between the spectra and data from different crystal models, we test various models for hydrogen incorporation. The only significant differences between orthoenstatite and low-clinoenstatite spectra relate to anisotropy of the higher wavenumber bands, which implies a change in orientation of longer OH dipoles between the two structures. High-pressure clinoenstatite reverts to low-clinoenstatite during depressurization, but subtle differences are noted between IR spectra of samples synthesized in the high-pressure clinoenstatite and low-clinoenstatite stability fields. Differences probably relate to the splitting of oxygen sites into two sets of non-equivalent sites during transformation of high-pressure clinoenstatite. The most realistic models for hydrogen incorporation into all three polymorphs involve association of hydrogen with the underbonded O2a and O2b sites. However, changes in OH dipole orientation between the different polymorphs and the effects of phase transitions on water solubility in the system MgSiO₃ mean the effects and implications of hydrogen incorporation into the three polymorphs may differ considerably.

Keywords: Enstatite, transition, hydrogen, water, mantle

INTRODUCTION

Over the last few decades, numerous investigations have demonstrated that significant amounts of “water” may be stored in nominally anhydrous minerals (NAMs) and phases that constitute the Earth’s mantle (Bell and Rossman 1992; Bolfan-Casanova et al. 2000; Ingrin and Skogby 2000). Water is stored in such phases as hydrogen structurally bound to specific oxygen sites, forming spectroscopically active OH groups. Hydrogen contents of NAMs vary from a few tens of parts per million to several weight percent H₂O, and NAMs provide a mechanism for storing significant amounts of water in different parts of the Earth’s mantle. Hydrogen incorporation into NAMs may play an important role in many mantle processes (e.g., Bercovici and Karato 2003), and may influence a range of mineral and bulk mantle properties as diverse as electrical conductivity and rheology (e.g., Huang et al. 2005; Mackwell et al. 1985).

Orthopyroxenes are major constituents of the upper mantle, and investigations of mantle xenoliths demonstrate that natural pyroxenes can contain up to thousands ppm H₂O wt (Ingrin and Skogby 2000). Numerous experimental investigations have focused on determining mechanisms for hydrogen incorporation into pure MgSiO₃ orthoenstatite, orthoenstatite doped with Al₂O₃, Fe₂O₃, and Cr₂O₃, and natural orthopyroxene annealed at high-pressure (Mierdel and Keppler 2004; Rauch and Keppler 2002; Stalder and Skogby 2002; Stalder 2004). These studies demonstrate that hydrogen incorporation into MgSiO₃ enstatite is charge-balanced by Mg²⁺ vacancies. In more complex systems, hydrogen incorporation may also be connected to coupled substitutions involving trivalent cations, and hydrogen solubility in pyroxene is greatly enhanced by the presence of Al³⁺. However, precise information on hydrogen positions in orthopyroxenes is lacking. Near-infrared spectra (NIR) from hydrogen-bearing orthopyroxenes are characterized by the presence of a significant number of OH stretching bands at frequencies ranging from 2800 to 4000 cm⁻¹, implying the presence of hydrogen in several non-equivalent sites. The difficulty of assigning OH absorption bands in NIR spectra from pyroxenes is further compounded by many potential hydrogen sites in pyroxene structures, and sometimes also from a lack of good quality polarized infrared absorption data.

Over the variable P-T conditions of the upper mantle the occurrence of several polymorphs of MgSiO₃ has been demonstrated [see Ulmer and Stalder (2001) for a recent review]. Over a broad range of temperatures up to pressures of between 6 and 10 GPa, MgSiO₃ has an orthorhombic Pbca structure (orthoenstatite). Toward lower temperatures, orthoenstatite transforms to P2₁/c clinoenstatite (low-clinoenstatite). With increasing pressure, both low-clinoenstatite and orthoenstatite transform to C2/c clinoenstatite (high-pressure clinoenstatite). This high-pressure structure is non-quenchable, and reverts to low-clinoenstatite. The orthoenstatite and low-clinoenstatite structures can be derived from each other by displacing alternat-
rahedral chains. In low-clinoenstatite, there are two different configurations, whereas in high-pressure clinohedrite there is only one configuration (Mendelssohn and Price 1997). All three enstatite polymorphs are structurally quite similar, and hydrogen is probably incorporated in each via similar mechanisms, and at similar sites. Transitions between the three polymorphs are accompanied by slight changes in O-O distances throughout the pyroxene structure. In this study, we compare polarized IR spectra obtained from different enstatite polymorphs, and use changes in O-O distances to provide detailed information on viable H positions in orthoenstatite and clinoenstatite.

**EXPERIMENTAL METHOD**

**Sample synthesis**

Enstatite samples were synthesized using a stoichiometric mixture of high-purity Mg(OH)₂ and SiO₂. Material was loaded into Pt capsules with approximately 10 wt% distilled H₂O and 5 wt% high purity SiO₂, which were then welded shut. Additional SiO₂ was added to compensate for the solubility of silica in water at elevated P-T and to ensure that in all experiments enstatite samples were grown under silica-saturated conditions. Synthesis experiments up to 4 GPa were performed using end-loaded piston-cylinder apparatus. At higher pressures, experiments were performed using Kawai-type split-sphere multi-anvil apparatus. For piston-cylinder experiments, 10 mm long, 5 mm outer diameter, 4.6 mm inner diameter capsules were used. Loaded capsules were placed into pyrophylite sleeves and then placed in 0.5″ tace-pyrex piston-cylinder assemblies containing internal, tapered, graphite resistance furnaces. Full details of pressure and temperature calibration are given in Bromiley and Keppler (2004). Experiments were pressurized to within 90% of the desired run pressure and then heated at 100 °C/min to 700 °C, before being fully pressurized. Pressure and temperature were continually monitored and maintained throughout the runs. For multi-anvil experiments, capsules were made from 2 mm outer diameter, 1.8 mm inner diameter Pt tubing. Capsules were loaded, welded shut, and then hammered using a pin press to a final length of 3.5 mm. Capsules were loaded into MgO ceramic octahedra with internal, stepped, LaCrO₃ resistance furnaces. 18 M Tohoku-grade WC anvils were used. Further details of pressure and temperature calibration are given in Bromiley and Keppler (2004).

Samples were fully pressurized and then heated at 100 °C/min to the final run temperature. Both multi-anvil and piston-cylinder experiments were isobarically quenched by switching off power to the heating circuits. After recovery, capsules were pierced to check for the presence of water. Runs in which a free fluid phase was not noted in recovered capsules were discarded.

For experiments to synthesize enstatite crystals large enough to be oriented and prepared for polarized IR work, runs were first heated to a temperature exceeding the melting point of the bulk composition and left for 1 h to equilibrate. Run temperatures were then lowered at approximately 30°C/min while maintaining run pressure. Run temperatures were then maintained at a final value for several hours. Bromiley and Keppler (2004) demonstrated that this technique is successful in producing large (up to several hundred micrometers) pyroxene crystals, presumably by destroying many of the potential sites for nucleation inside the capsule. In all experiments, phases were identified optically and by X-ray diffraction. Polymorphs of enstatite were identified using a Dilor labram Raman spectrometer equipped with a 20 mW HeNe laser and a microscope, using criteria outlined by Ulmer and Stalder (2001). For runs in which samples were too small to be oriented, doubly polished 30–50 µm thick sections were prepared from capsules using CRYSTALBOND. Sections were removed from glass slides by soaking in high-purity acetone for 48 h.

For higher temperature runs, crystals were large enough to be oriented using X-ray techniques. Orthoenstatite crystals were oriented using a precession camera to within an accuracy of ±1°. Clinoenstatite crystals were oriented using a Huber 511.1 four-circle single-crystal diffractometer and an XCALIBUR Oxford Instruments diffractometer. Crystals were mounted in UV epoxy resin before being prepared as doubly polished sections up to 200 µm thick (for orthoenstatite) and up to 50 µm thick (for clinoenstatite). Crystal orientation was then rechecked after polishing, and the directions of two of the crystallographic axes lying in the plane of the slab determined. Slabs of crystals were then re-polished to produce edges parallel to these two axes. Slabs were soaked in high-purity acetone for at least 24 h.

**RESULTS**

Run conditions are listed in Table 1. In all experiments, enstatite was the main run product, with small amounts of additional coesite. In experiments Hen1 and Hen2, crystals were large enough to be oriented using X-ray techniques, and polarized IR spectra could be obtained. For all other experiments, crystals were too small to be oriented, and unpolarized spectra were obtained. Raman spectra and XRD data confirm that samples synthesized in the high-pressure clinoenstatite stability field reverted to low-clinoenstatite during depressurization. Polarized NIR spectra from orthoenstatite and clinoenstatite are shown in Figures 1 and 2, respectively, and unpolarized spectra in Figure 3. Data on OH stretching absorption bands in both sets of spectra are listed in Tables 2 and 3, respectively.

**DISCUSSION**

**Polarized spectra**

Polarized spectra obtained from orthoenstatite (Fig. 1) are essentially the same as spectra from orthoenstatite synthesized at 1000 °C, 1.5 GPa by Mierdel and Keppler (2004). Spectra are dominated by two sharp OH absorption bands at 3361 and 3381 cm⁻¹. The bands are associated with vibrations in the OH groups of water molecules that are hydrogen-bonded to the pyroxene lattice. The IR spectra are dominated by two sharp OH absorption bands at 3361 and 3381 cm⁻¹. The bands are associated with vibrations in the OH groups of water molecules that are hydrogen-bonded to the pyroxene lattice. The IR spectra are dominated by two sharp OH absorption bands at 3361 and 3381 cm⁻¹. The bands are associated with vibrations in the OH groups of water molecules that are hydrogen-bonded to the pyroxene lattice.
Spectra also consist of several additional, smaller absorption bands at higher wavenumbers. This is in contrast to spectra from orthoenstatite published by Rauch and Keppler (2002) and Stalder and Skogby (2002), which only contain one sharp absorption band around 3361 cm\(^{-1}\) in addition to the broad band around 3065 cm\(^{-1}\). Stalder (2002, 2004) suggested that the appearance of additional absorption bands in IR spectra from orthopyroxene is due to hydrogen incorporation coupled to the presence of additional trivalent cations, mainly aluminum. However, all samples synthesized in this investigation and by Mierdel and Keppler (2004) are pure MgSiO\(_3\), so this cannot be the case. Instead, Mierdel and Keppler (2004) note that there is a strong influence of synthesis temperature on hydrogen incorporation into quenched orthoenstatite, with some absorption bands not easily discernable at lower or higher temperatures of synthesis. Appearance of additional OH absorption bands in polarized spectra in this study compared to previous studies is probably also due to better spectral resolution, which, for example, makes it easier to resolve the separate absorption bands at 3361 and 3381 cm\(^{-1}\). The appearance of additional OH bands in spectra from orthoenstatite doped with Al\(_2\)O\(_3\) (Stalder and Skogby 2002) could simply be due to better spectral resolution in samples with much higher overall water contents.

Polarized spectra from clinoenstatite (Fig. 2) share many similar features with orthoenstatite spectra shown in Figure 1, including a large absorption band at 3376 cm\(^{-1}\), and an unusual, broad band at 3065 cm\(^{-1}\). Spectra also consist of several additional, smaller absorption bands at higher wavenumbers. This is in contrast to spectra from orthoenstatite published by Rauch and Keppler (2002) and Stalder and Skogby (2002), which only contain one sharp absorption band around 3361 cm\(^{-1}\) in addition to the broad band around 3065 cm\(^{-1}\). Stalder (2002, 2004) suggested that the appearance of additional absorption bands in IR spectra from orthopyroxene is due to hydrogen incorporation coupled to the presence of additional trivalent cations, mainly aluminum. However, all samples synthesized in this investigation and by Mierdel and Keppler (2004) are pure MgSiO\(_3\), so this cannot be the case. Instead, Mierdel and Keppler (2004) note that there is a strong influence of synthesis temperature on hydrogen incorporation into quenched orthoenstatite, with some absorption bands not easily discernable at lower or higher temperatures of synthesis. Appearance of additional OH absorption bands in polarized spectra in this study compared to previous studies is probably also due to better spectral resolution, which, for example, makes it easier to resolve the separate absorption bands at 3361 and 3381 cm\(^{-1}\). The appearance of additional OH bands in spectra from orthoenstatite doped with Al\(_2\)O\(_3\) (Stalder and Skogby 2002) could simply be due to better spectral resolution in samples with much higher overall water contents.

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TABLE 3. Characteristics of OH stretching absorption bands in polarized NIR spectra from H-bearing MgSiO$_3$ low clinoenstatite $P2_1/c$ (transformed from high-pressure clinoenstatite, C2/c)

<table>
<thead>
<tr>
<th>Wavenumber (cm$^{-1}$)</th>
<th>Characteristics</th>
<th>Band anisotropy$^*$</th>
</tr>
</thead>
<tbody>
<tr>
<td>3668</td>
<td>sharp</td>
<td>a$^*$&gt;&gt;c=b</td>
</tr>
<tr>
<td>3676</td>
<td>very sharp</td>
<td>a$^*$&gt;&gt;c=b</td>
</tr>
<tr>
<td>3656</td>
<td>very small</td>
<td>a$^*$&gt;&gt;c=b</td>
</tr>
<tr>
<td>3635</td>
<td>small and broad</td>
<td>a$^*$&gt;&gt;c=b</td>
</tr>
<tr>
<td>3601</td>
<td>large, asymmetric (due to shoulder at slightly higher wavenumber?)</td>
<td>a$^<em>$&gt;&gt;c=b; c$^</em>$</td>
</tr>
<tr>
<td>3573</td>
<td>very small</td>
<td>a$^*$&gt;&gt;c=b</td>
</tr>
<tr>
<td>3555</td>
<td>small</td>
<td>a$^*$&gt;&gt;c=b</td>
</tr>
<tr>
<td>3510</td>
<td>small and broad</td>
<td>b$^*$&gt;&gt;c</td>
</tr>
<tr>
<td>3503</td>
<td>small and broad</td>
<td>c$^<em>$&gt;&gt;a$^</em>$, b=0</td>
</tr>
<tr>
<td>3491</td>
<td>sharp</td>
<td>b$^<em>$&gt;&gt;a$^</em>$&gt;&gt;c</td>
</tr>
<tr>
<td>3474</td>
<td>small</td>
<td>a$^*$&gt;&gt;b=c</td>
</tr>
<tr>
<td>3376</td>
<td>large band</td>
<td>c$^<em>$&gt;&gt;a$^</em>$&gt;&gt;b</td>
</tr>
<tr>
<td>3282</td>
<td>small, very broad</td>
<td>b$^<em>$&gt;&gt;a$^</em>$&gt;&gt;c</td>
</tr>
<tr>
<td>3042</td>
<td>unusual broad, asymmetric band</td>
<td>c$^*$&gt;&gt;b</td>
</tr>
<tr>
<td>2927</td>
<td>small broad band</td>
<td>a$^*$=c, b=0</td>
</tr>
<tr>
<td>2855</td>
<td>small broad band</td>
<td>a$^*$=c, b=0</td>
</tr>
</tbody>
</table>

$^*$ Orientation of OH band determined from polarized spectra, where > means "greater than," >> means "much greater than," and // means "approximately parallel to."

strong component of vibration parallel to the crystallographic $c$ axis, a broad absorption band at 3042 cm$^{-1}$, and several sharp OH absorption bands at higher wavenumbers. Mierdel and Keppler (2004) suggested that the absorption band at 3381 cm$^{-1}$ in orthoenstatite spectra corresponds to the main OH band in clinoenstatite spectra, implying hydrogen incorporation into the orthoenstatite related to the presence of lamellae of a monoclinic phase (i.e., lamellae with a low-clinoenstatite type structure). However, careful comparison of the orthoenstatite and clinoenstatite spectra shown in Figure 4 demonstrates that this is not the case, and that the main clinoenstatite OH absorption band is actually at 3376 cm$^{-1}$.

Unpolarized spectra

Unpolarized spectra were obtained from samples synthesized at 700 °C, from 5.5 to 8.0 GPa (Fig. 4). Although the high-pressure clinoenstatite structure transforms to low-clinoenstatite during depressurization, this series of experiments allows comparison between IR spectra from low-clinoenstatite (Lcen) and high-pressure clinoenstatite that has transformed to low clinoenstatite during depressurization (H-Lcen).

Results of micro-Raman and XRD analysis of run products reveal that sample Hen3 is orthoenstatite. IR spectra from this sample are similar to polarized NIR spectra obtained from orthoenstatite (Fig. 3), although there are some differences in relative band intensities. In contrast, all other spectra resemble clinoenstatite spectra. Therefore, it is possible to use NIR spectra to differentiate between orthoenstatite and clinoenstatite. Figure 4 also demonstrates clear differences between IR spectra obtained from clinoenstatite synthesized at 6.0 GPa and clinoenstatite synthesized at higher pressure. All spectra from higher-pressure samples are similar, which suggests that this difference is not simply due to some pressure dependence of relative OH band height. Instead, it is more likely that differences arise from the fact that sample Hen4 was synthesized in the low-clinoenstatite stability field and that other higher-pressure samples were synthesized in the high-pressure clinoenstatite stability field. This is consistent with both MD modeling and experimental studies of the stability of MgSiO$_3$ polymorphs (Mendelsohn and Price 1997; Shimmi et al. 1999).

**OH band assignment**

Using data on absorption band anisotropy and the relationship between OH stretching frequencies and O-O distances (Libowitzky 1999; Nakamoto et al. 1955), it is possible to assign OH absorption bands in NIR spectra to specific oxygen sites in the host structure (e.g., Bromiley et al. 2004). This assumes that OH groups are approximately co-linear with oxygen sites adjacent to cation vacancies, an extreme example of this being the hydrogarnet substitution mechanism (Lager et al. 1987). Rauch and Keppler (2002) demonstrated that hydrogen incorporation into enstatite is charge-balanced by Mg$^{2+}$ vacancies, and it is likely that in ortho- and clinoenstatite at least some hydrogen will be associated with oxygen sites surrounding vacant cation sites (most likely M2). The problem of OH band assignment is further compounded by the complexity of enstatite structures, which means that there are a large number of potential hydrogen sites to choose from. Here, we adopt the novel approach of using changes in O-O distances between enstatite polymorphs, which can be correlated with changes in O-H stretching frequencies, to test models for H incorporation. This approach is validated by similarities between crystal structures and IR spectra for the different polymorphs. For testing this approach, we use data on atomic coordinates in MgSiO$_3$ orthoenstatite at ambient pressure from Hugh-Jones and Angel (1994) and Yang and Ghose (1995), and data on low-clinoenstatite from an idealized MgSiO$_3$ $P2_1/c$ clinoenstatite at ambient conditions by Thompson and Downs (2004), from a Cr$^{3+}$-bearing clinopyroxene from Angel et al. (1989), and data on Ca$_{0.15}$Mg$_{0.85}$Si$_2$O$_6$ $P2_1/c$ low-clinoenpyroxene from Tribaudino et al. (2002). For comparison of the low-clinoenstatite and high-pressure clinoenstatite structures we use the crystal models from Nestola et al. (2004), who investigated the $P2_1/c$ to $C2/c$ transition in a low-Ca pigeonite.
In addition to published frequency-distance correlations and observed anisotropy, we draw upon structural considerations of bond strength. Pauling (1929) defined the bond strength sum of an anion as the sum of the fractional charges from the bonded cations (the ionic valence of each cation divided by its coordination). Due to charge balance requirements, the bond strength sum for oxygen sites in oxides and silicates almost always equals the negative valence of the anion. In high-pressure clinoenstatite, there are three different oxygen sites, and in orthoenstatite and low-clinoenstatite, each of these three sites is split into two non-equivalent sites: two “normal” oxygen sites that are coordinated to one T-site and three M-sites (O1a and O1b) with a bond strength sum of 2.0, two “underbonded” oxygen sites coordinated to one T-site and two M-sites (O2a and O2b) with a bond strength sum of 1.5/3, and two “overbonded” oxygen sites (O3a and O3b) coordinated to two T-sites and one M-site with a bond strength sum of 2.1/3. The overbonded O3 sites are bridging oxygen of the silicate chain and therefore the least likely candidates for hydrogen.

3361 and 3381 cm⁻¹ bands in orthoenstatite and 3376 cm⁻¹ band in clinoenstatite spectra

Rauch and Keppler (2002) assigned the band at 3361 cm⁻¹ in orthoenstatite spectra to hydrogen associated with O2b. The O2b site is non-bridging and highly underbonded, and is the most likely O atom for hydrogen association, along with the structurally similar O2a site. Vibration of OH groups approximately parallel to the crystallographic c axis would imply vibration toward an adjacent O1b atom along the edge of one of the M1 sites (i.e., O2b-O1b, M1), or toward an O1b atom along the edge of an M2 site (O2b-O1b, M2). The O-O distances of these two sites are around 3.0 Å, which is slightly greater than distances calculated from O-H stretching frequencies (approximately 2.8 Å), although this difference could be explained by hydrogen docking close to a Mg vacancy. The difference in O-O distances between the two sites is approximately 0.1 Å, corresponding to a difference in OH stretching frequencies of around 30 cm⁻¹, which corresponds well with the actual difference between the two main OH bands in orthoenstatite spectra at 3361 and 3381 cm⁻¹. Therefore, the band at 3361 cm⁻¹ could correspond to vibration of an OH dipole close to (O2b-O1b, M2), and the band at 3381 cm⁻¹ to vibration of an OH dipole close to (O2b-O1b, M1). Close examination of orthoenstatite spectra reveals that the 3361 and 3381 cm⁻¹ absorption bands are quite distinct, because they exhibit slightly different anisotropies. The band at 3361 cm⁻¹ has a much lower component of vibration parallel to the crystallographic c axis, and a higher component of vibration parallel to the b axis compared to the band at 3381 cm⁻¹.

In low-clinoenstatite the (O2b-O1b, M2) distance is increased slightly and the (O2b-O1b, M1) distance decreased slightly relative to orthoenstatite. This corresponds to a slight shift in stretching frequencies of the 3361 and 3381 cm⁻¹ bands to higher and lower frequencies, respectively. Therefore, the 3376 cm⁻¹ clinoenstatite band may actually correspond to either of the 3361 and 3381 cm⁻¹ orthoenstatite bands, implying that only one of these sites can incorporate hydrogen in the clinoenstatite structure. Alternatively, OH bands corresponding to hydrogen incorporated at both sites may be close enough to overlap significantly, implying that both mechanisms operate and that the 3376 cm⁻¹ clinoenstatite band is an unresolved doublet.

In contrast to the OH band assignment described above, Stalder and Skogby (2002) suggested that the OH band at 3361 cm⁻¹ in orthoenstatite spectra was due to vibration of an OH dipole co-linear with O3b-O3b, with an O-O distance closer to the predicted value to 2.8 Å. However the O3b-O3b distance is slightly shorter in low-clinoenstatite than in orthoenstatite, which should correspond to a shift in the OH band at 3361 cm⁻¹ to lower wavenumbers, the opposite to what is actually observed.

3065 cm⁻¹ band in orthoenstatite and 3042 cm⁻¹ in clinoenstatite spectra

The nature of this unusual, broad asymmetric absorption band is unclear, and it could either be due to OH stretching or some type of mixed phonon process. Stalder and Skogby (2002) assigned this band to hydrogen associated with O3a, with vibration of the OH dipole toward another O3A site along a tetrahedral edge (O3a-O3a, T). This would appear unlikely because of the overbonded nature of the O3a site. A more likely hydrogen incorporation mechanism would be (O2b-O3b, T), with hydrogen associated with the underbonded O2b site. Unfortunately, there are no consistent trends in O-O distances for these sites between the two polymorphs, so we are unable to test these assignments.

Higher wavenumber bands in orthoenstatite spectra

The orthoenstatite spectra shown in Figure 1 also contain several additional absorption bands at higher wavenumbers, the most important being those at 3475 and 3548 cm⁻¹. These bands have strong components of vibration parallel to the crystallographic c axis, and could be due to hydrogen associated with the underbonded O2a, with vibration of OH dipoles toward adjacent O1a sites, either along M1 octahedral or M2 polyhedral edges. Hydrogen incorporated at these sites would result in OH absorption bands around 3550 cm⁻¹ for the M1 edge, and 3520 cm⁻¹ for the M2 edge. This corresponds well with observed spectra, and we can tentatively assign absorption bands at 3549 and 3475 cm⁻¹ to OH dipoles close to (O2a-O1a, M1) and (O2a-O1a, M2), respectively. Predicted OH stretching frequencies for these bands are close to observed values, implying OH dipoles are not associated with Mg²⁺ vacancies, in contrast to the bands at 3361 and 3381 cm⁻¹.

Higher wavenumber bands in low-clinoenstatite spectra

From Figure 2 it is evident that orthoenstatite OH bands at 3548 and 3475 cm⁻¹ do not have corresponding bands in the clinoenstatite spectra, implying that for higher wavenumber OH bands, there are significant differences between hydrogen incorporation mechanisms in orthoenstatite and low-clinoenstatite. In both structures, O2a and O2b sites are the most likely hosts for hydrogen incorporation, so these differences could simply be due to a change in orientation of longer OH dipoles. In low-clinoenstatite, H incorporated close to O2a could vibrate toward a neighboring O3b site (O2a-O3b, M2). This would produce an OH dipole with a strong component of vibration parallel to the crystallographic c axis, and a wavenumber around 3570 cm⁻¹.
This could account for the OH absorption band at 3601 cm\(^{-1}\) in clinoenstatite spectra. This assignment is further supported by the fact that during IR measurements, we noted that the 3601 cm\(^{-1}\) band has a stronger component of vibration parallel to the \(a^*\) axis than the \(a^x\) axis. This mechanism is comparable to H incorporation close to (O2a-O1a, M2) in orthoenstatite. The reason for a possible change in orientation of O2a-H dipoles between the orthoenstatite and clinoenstatite structures is not clear, but could be related to relative changes in O-O distances around the M2 site.

The OH absorption band at 3548 cm\(^{-1}\) in the orthoenstatite spectra was tentatively assigned to hydrogen incorporated close to (O2a-O1a, M1). However, in this instance, a simple change in orientation of the OH dipole cannot be inferred, because none of the O-O edges surrounding the M1 site in the low-clinoenstatite provide suitable hydrogen incorporation mechanisms. In contrast, reorientation of O2b-H dipoles does appear possible. One possible site for hydrogen incorporation is (O2b-O3a, M2), corresponding to a calculated OH band wavenumber of around 3590 cm\(^{-1}\). The predicted nature of the corresponding OH absorption band is again close to that of the observed band at 3601 cm\(^{-1}\). If correct, this would imply that the 3376 cm\(^{-1}\) OH band in the clinoenstatite spectra is only due to hydrogen incorporated on the (O2b-O1b, M1) edge (i.e., equivalent to the 3381 cm\(^{-1}\) band in orthoenstatite spectra). Alternatively, hydrogen could be incorporated close to O2b but on one of the M1 edges. The most likely site in this instance would be (O2b-O2a, M1), corresponding to an OH band around 3500 to 3530 cm\(^{-1}\). In terms of oxygen overbonding, this site would appear more favorable because both O2b and O2a sites are significantly underbonded. In contrast, the O3a site is a bridging oxygen, and is significantly overbonded. However, hydrogen incorporated on (O2b-O2a, M1) would result in OH dipoles with a stronger component of vibration parallel to the \(a^*\) axis compared to the \(a\) axis, which is the opposite relationship to that observed in polarized spectra from clinoenstatite for the higher wavenumber OH bands, except the small band at 3491 cm\(^{-1}\).

It should be noted that for orthoenstatite, there is a large discrepancy between calculated OH band wavenumbers based on O2b-O1b (M1 and M2 edge) distances and actual stretching frequencies. This was inferred to be the result of coupling of OH groups with Mg\(^{2+}\) vacancies. A similar effect would be predicted for both clinoenstatite polymorphs. Furthermore, for OH bands with higher wavenumbers, assignment to particular O-O distances is much more difficult because of the nature of the O-O distance vs. O-H stretching frequency calibration. For the two highest wavenumber OH bands in the clinoenstatite spectra at 3688 and 3676 cm\(^{-1}\), no direct assignment is possible using the method outlined above. Examination of different low-clinoenstatite crystal models does not readily reveal any O-O sites that could account for these high wavenumber bands.

**Higher wavenumber bands in (transformed) high-pressure clinoenstatite spectra**

The two mechanisms proposed to explain the low-clinoenstatite OH band at 3601 cm\(^{-1}\) involve hydrogen located close to (O2a-O3b, M2) and (O2b-O3a, M2). In high-pressure clinoenstatite, oxygen sites are not split and these two edges become equivalent, i.e., (O2-O3, M2). This represents a decrease in O-O distances between the two structures of about 0.09 and 0.57 Å, respectively. The 3601 cm\(^{-1}\) OH band is much stronger in LCen spectra compared to H-LCen spectra, implying that the hydrogen incorporation mechanism is significantly less favorable in the high-pressure structure. This might suggest that the 3601 cm\(^{-1}\) band corresponds to hydrogen incorporated close to the (O2b-O3a, M2) edge because the difference in O-O distances between the two clinoenstatite polymorphs for this edge is greater. Alternatively, differences in absorption band height could reflect differences in the number of cation vacancies in the two polymorphs, which provides the means for charge-balancing hydrogen incorporation.

### 3492 and 3474 cm\(^{-1}\) bands in clinoenstatite spectra

Another noticeable difference between Lcen and H-Lcen spectra is that the OH band at 3492 cm\(^{-1}\) is much stronger in Lcen spectra, and that in H-Lcen spectra, a small additional band at 3474 cm\(^{-1}\) is present. The band at 3492 cm\(^{-1}\) has a markedly different anisotropy to other OH bands, with a strong component of vibration parallel to the crystallographic \(b\) axis. The OH band at 3474 cm\(^{-1}\) is smaller, and the anisotropy more difficult to ascertain. Hydrogen incorporation on either of two different O-O edges could explain the nature of the OH band at 3492 cm\(^{-1}\). First, hydrogen could be incorporated on the (O2b-O1b, M1) edge, corresponding to an OH stretching frequency of 3430–3580 cm\(^{-1}\). A second possibility is hydrogen incorporation close to (O2a-O1a, M1), corresponding to an OH stretching frequency of 3530–3550 cm\(^{-1}\). Both of these O-O edges are parallel to the crystallographic \(b\) axis. The OH band at 3492 cm\(^{-1}\) has a significant component of vibration parallel to \(a^*\) axis, implying that OH groups incorporated on either of these sites would have to vibrate at a significant angle from each O-O edge. In high-pressure clinoenstatite these two potential hydrogen sites become equivalent (O2-O1, M1). This results in an effective increase in the (O2a-O1a, M1) distance, and a decrease in the (O2b-O1b, M1) distance during the low-clinoenstatite to high-pressure clinoenstatite phase transition. In fact, this could explain some of the differences between spectra from H-Lcen and Lcen. If we assume that in high-pressure clinoenstatite structure hydrogen is incorporated close to (O2-O1, M1) then during transformation to the low-clinoenstatite structure and splitting of oxygen sites, some hydrogen may end up on (O2a-O1a, M1) and some on the slightly longer (O2b-O1b, M1) site. The difference in O-O distances between these sites, depending on different crystal models, ranges from 0 to 0.14 Å, corresponding to a difference in OH stretching frequency of up to 30 cm\(^{-1}\). This corresponds well to the observed difference in stretching frequency between the two small bands at 3492 and 3474 cm\(^{-1}\). Therefore, the OH bands at 3492 and 3474 cm\(^{-1}\) could correspond to hydrogen incorporated close to the (O2b-O1b, M1) and (O2a-O1a, M1) edges in H-Lcen, respectively. In contrast, only the band at 3491 cm\(^{-1}\) is present in the Lcen structure, which would imply that hydrogen incorporation on the slightly longer (O2b-O1b, M1) site in low-clinoenstatite is more favorable.
**Implications of Hydrogen Incorporation into Enstatite**

NIR spectra from orthoenstatite, low-clinoenstatite, and high-pressure clinoenstatite (transformed to low-clinoenstatite) share some common features due to structural similarities. However, important differences between NIR spectra are noted for higher wavenumber OH bands. In orthoenstatite spectra, all major OH bands have strong components of vibration parallel to the crystallographic c axis. In contrast, most of the higher wavenumber bands in clinoenstatite spectra have much stronger components of vibration parallel to a* axis. These differences could be important because in clinoenstatite a much greater proportion of hydrogen is incorporated on sites corresponding to these higher wavenumber bands compared to orthoenstatite. In fact, in spectra from the only sample synthesized in the low-clinoenstatite stability field nearly all hydrogen is incorporated on sites corresponding to these OH bands. Different orientations of OH dipoles in the three enstatite polymorphs could result in differences in the effects of hydrogen incorporation on properties as diverse as electrical conductivity and deformation mechanisms. In particular, mechanisms for hydrogen incorporation could, conceivably, influence mechanisms for phase transformations between enstatite polymorphs. For example, the low-clinoenstatite to orthoenstatite transformation can be represented as a displacement of octahedral and tetrahedral layers relative to the crystallographic c axis. Polarized IR spectra of orthoenstatite demonstrate that all hydroxyl groups have a strong component of vibration parallel to c, and hydrogen incorporation is unlikely to have a significant effect on the transformation to low-clinoenstatite. By contrast, most of the OH groups in low-clinoenstatite vibrate approximately parallel to the a* axis, and so hydrogen incorporation into low-clinoenstatite could, conceivably, affect the displacive transition to the orthoenstatite structure with increasing temperature.

In all three polymorphs, the most likely mechanisms for hydrogen incorporation involve highly underbonded O2 sites, which are split into two sets of non-equivalent sites in the orthoenstatite and low-clinoenstatite structures. OH band assignments indicate that some hydrogen may be incorporated close to O atoms surrounding vacant cation sites. In contrast, for other proposed incorporation mechanisms, good agreement between calculated OH stretching frequencies and observed values suggest that some hydrogen may be incorporated close to oxygen sites not related to cation vacancies. This could have important implications for relative rates of hydrogen diffusion in enstatite, with fast diffusion of hydrogen due simply to hopping of interstitial hydrogen through the crystal structure (coupled to fast electron transfer), and much slower diffusion of hydrogen coupled to diffusion of Mg²⁺ vacancies. Furthermore, differences in orientation of OH dipoles between the different enstatite polymorphs would be expected to affect rates of hydrogen diffusion along different crystallographic directions.

In an investigation of hydrogen solubility in enstatite as a function of pressure, Rauch and Keppler (2002) noted a drop in water solubility across the orthoenstatite to high-pressure clinoenstatite transition. They suggested that this was not due to any difference in solubility between the two structures, but was only due to a trend in changing water contents as a function of pressure over the whole pressure range from 0.5 to 10 GPa. Actual comparison of water/hydrogen contents in different enstatite polymorphs determined from IR data is problematic at best because of a lack of suitable (i.e., sample specific) calibrations for low- and high-pressure clinoenstatite. Furthermore, differences between hydrogen incorporation mechanisms in the different polymorphs mean that it is also difficult to compare water contents determined using general calibrations. However, data can be used to identify general trends in water solubility, and may be of some use in initial determinations of hydrogen partitioning. Water contents of samples synthesized in the present study, determined using the general calibration of Paterson (1982), are listed in Table 1. Data suggest that at 700 °C, water solubility in low-clinoenstatite is considerably higher than in orthoenstatite. This is probably due to the large number of OH bands in the low-clinoenstatite spectra at higher wavenumbers. According to the Paterson (1982) calibration, OH bands at higher wavenumbers correspond to larger amounts of water than bands with similar intensities at lower wavenumbers. Furthermore, data suggest that at 700 °C, water solubility in low-clinoenstatite is over three times higher than in orthoenstatite. Differences in water solubility between the polymorphs at this temperature are unlikely to represent some simple effect of pressure because of the large changes in values over a relatively small pressure range. This implies a real difference in water solubility between the three polymorphs, which could be due to changes in O-O distances and/or some change in the number of Mg²⁺ vacancies. H partitioning between the polymorphs could increase the stability of low-clinoenstatite to slightly higher temperatures (i.e., relative to the stability of orthoenstatite), and to higher pressures (i.e., relative to the stability of high-pressure clinoenstatite). The effects of phase transitions on water solubility in the system MgSiO₃ also mean that some care needs to be taken when applying data on the effects of water solubility in orthoenstatite to the whole mantle.

NIR spectra from samples synthesized in the low-clinoenstatite and high-pressure clinoenstatite stability fields reveal, for the first time, subtle differences between the quenched samples. These differences allow the low-clinoenstatite to high-pressure clinoenstatite phase transition to be bracketed at high P-T using quench experiments. Unfortunately, because of the stability of talc and the 10 Å phase (Chinnery et al. 1999), this transition cannot be bracketed at temperatures much lower than 700 °C. It is also not certain whether NIR spectra could be used to differentiate between naturally occurring low and high-pressure clinoenstatite because of the rapid diffusivity of hydrogen, resulting in rapid re-equilibration of water contents and hopping of hydrogen to more favorable interstitial sites.

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