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Title
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Permalink
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Journal
Journal of Geophysical Research: Solid Earth, 122(8)

ISSN
2169-9313

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Publication Date
2017-08-01

DOI
10.1002/2017JB014344

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Peer reviewed
The high-pressure phase of lawsonite: A single crystal study of a key mantle hydrous phase

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Abstract

Lawsonite CaAl$_2$Si$_2$O$_7$(OH)$_2$·H$_2$O is an important water carrier in subducting oceanic crusts, and the primary hydrous phase in basalt at depths greater than ~80 km. We have conducted high-pressure synchrotron single-crystal x-ray diffraction experiments on natural lawsonite at room temperature up to ~10.0 GPa to study its high-pressure polymorphism. We find that lawsonite remains orthorhombic with Cmcm symmetry up to ~9.3 GPa, and shows nearly isotropic compression. Above ~9.3 GPa, lawsonite becomes monoclinic with $P2_1/m$ symmetry. Across the phase transition, the Ca polyhedron becomes markedly distorted, and the average positions of the H$_2$O molecules and hydroxyls change. The changes observed in the H-atom positions under compression are different than the low temperature changes in this material. We resolve for the first time the H-bonding configuration of the high-pressure monoclinic phase of lawsonite. A bond valence approach is deployed to determine that the phase transition from orthorhombic to monoclinic is primarily driven by the Si$_2$O$_7$ groups, and in particular it's bridging oxygen atom (O1). The changes in the structure strongly indicate that entropy increases across the symmetry-lowering transition, and hence that the slope of the phase transition is negative. Therefore, monoclinic lawsonite is thus stable under the pressure and temperature conditions that exist in the Earth, and is likely to be a major water carrier in colder, deep subducted slabs. Monoclinic lawsonite also likely has enhanced electrical conductivity along its c-axis due to the dynamically disordered hydrogen atoms.

Key words: Lawsonite; CaAl$_2$Si$_2$O$_7$(OH)$_2$·H$_2$O; Single-crystal diffraction; High-Pressure; Hydrogen disorder

1. Introduction
Significant amounts of water are transported into the mantle by subduction zones in the form of hydrated minerals in oceanic crust and continentally derived meta-sediments [Ono, 1998; Chinnery et al., 2000; Dobrzynetskaya and Green, 2007]. This water affects the chemical and physical properties of materials by lowering their solidus temperatures, which allows for partial melting of mantle material at relatively low temperatures, and by altering rheological properties. Water reservoirs in subducted oceanic crust and its overlying sediments include chloritoid, lawsonite, topaz, serpentines, chlorite (clinochlore), zoisite, amphiboles and micas. Lawsonite is particularly interesting because of its high overall water content, ~11.5 wt.% [Baur, 1978], large stability field, and its prevalence in fully hydrated mid-ocean ridge basalt (MORB) at pressure, which contains 7-15 wt% lawsonite [Schmidt and Poli, 1998]. Lawsonite and phengitic mica are thought to be the dominant water carriers in subducted crust from ~200 to over 300 km depth, which corresponds to pressures of ~7-10 GPa [Pawley, 1994; Schmidt and Poli, 1994; Domanik and Holloway, 1996]. The way that H₂O molecules and OH groups are contained within the lawsonite structure is unusual (Figure 1). H₂O molecules reside in cavities that are formed by rings of two Si₂O₇ groups and two Al-octahedra. These cavities are not completely open channels, like the channels typically found in ring silicates (e.g. cordierite), but the channels in lawsonite also contain the large Ca ion, bound to the ring framework, in addition to the water molecule. The OH groups are contained within a much smaller channel in the structure formed by two AlO₆ octahedra and two SiO₄ tetrahedra.
Lawsonite undergoes two low temperature phase transitions at 155(5) and 273(5) K at ambient pressure that involve changes in the hydrogen bonding of the H$_2$O and OH groups [Libowitzky and Armbruster, 1995], and to a lesser extent changes in the aluminosilicate framework. However, no phase transitions are observed upon heating to ~600 °C [Pawley et al., 1996]. Notably, the H atoms of the H$_2$O and OHs in lawsonite are dynamically disordered and oscillate between two equivalent sites, and the low temperature phase transitions are interpreted to be generated by a freezing in of the dynamic hopping motions of the H atoms [Libowitzky and Armbruster, 1995; Libowitzky, 2009]. High pressure, room temperature single-crystal diffraction structures have been reported up to ~3.78 GPa [Comodi and Zanazzi, 1996].
and no phase transitions were reported in this pressure range. An additional phase transition at ~4 GPa from orthorhombic C to an orthorhombic P space group was reported by Boffa Ballaran and Angel (2003) using single-crystal diffraction, but they could not determine the structure and space group of this phase. At higher pressures, Scott and Williams (1999) reported a discontinuous shift in the O-H stretching vibrations at ~8-9 GPa in the high-pressure infrared spectra of lawsonite. Daniel et al. (2000) reported a phase transition at ~8.6 GPa using Raman spectroscopy and powder diffraction, and Pawley and Allan (2001) observed the same transition at ~10-11 GPa using powder diffraction. This transition, from orthorhombic to monoclinic symmetry, has now been known, for ~16 years, to occur between ~8.6 and ~11 GPa [Daniel et al., 2000; Pawley and Allan, 2001; Boffa Ballaran and Angel, 2003].

Structural determinations of the proposed orthorhombic P phase (> 4 GPa) and the monoclinic P phase have not been reported, and both of these transitions occur at pressures relevant to subduction zones. Pawley and Allan (2001) reported a Rietveld refinement of the $P2_1/m$ structure of monoclinic lawsonite using the orthorhombic $Cmcm$ structure as their starting model. The P-T slope of this phase transition is poorly constrained, and Pawley and Allan (2001) hypothesize that this transition has a shallow positive slope. If this were the case, the high-pressure phase of lawsonite would be unlikely to be stable under conditions found within subduction zones. However, Pawley and Allan (2001) also explicitly state that a negative slope cannot be ruled out, which would intersect the temperature field within colder subducted slabs. Moreover, the high-pressure phase of lawsonite almost certainly has higher entropy since the oxygen position, O2, splits into two separate sites in the monoclinic structure, O2A and O2B, and the cation site M1 splits into M1A and M1B (e.g. Liebscher et al., 2010; Pawley and
Hence, $\Delta S_{\text{ortho-mono}}$ is anticipated to be positive, and $\Delta V_{\text{ortho-mono}}$ is small but negative (e.g. Boffa Ballaran and Angel, 2003; Daniel et al., 2000; Pawley and Allan, 2001), which indicates that the slope of the $\text{Cmcm-P2}_1/m$ transition must be negative. From this it follows that the high-pressure monoclinic phase of lawsonite could be the dominant water carrier in basalts carried by rapidly subducted, older slabs, and thus may be of considerable importance for moving water to depths deeper than 300 km (~10 GPa), and approaching the top of the transition zone.

High quality single-crystal structural determinations for the high-pressure phase(s) of the dominant carrier of water to depths of ~300 km in subducted basalt [Schmidt and Poli, 1998] and in hydrated metamorphic assemblages associated with subduction [Vitale Brovarone and Beyssac, 2014] have thus not yet been reported, and the structure of this primary water carrier is uncertain. This study uses synchrotron based single-crystal x-ray diffraction at room temperature to examine the structural changes of lawsonite under compression up to ~10.0 GPa. The great benefit of single-crystal structure determinations is the ability to ab initio determine, and subsequently refine the atomic positions. Moreover, atomic positions can be refined with anisotropic displacement parameters (ADPs), which is often not possible based on the reduced data quality obtained by high pressure poeder diffraction. Here, our goals are to probe and characterize the existence of the proposed ~4.0 GPa transition in lawsonite, and solve the structure of the higher-pressure monoclinic lawsonite. Both the proposed orthorhombic P phase and the monoclinic P phase occur within pressure ranges that are important for our understanding of subduction zones, and both are thus anticipated to be primary carriers of water to depth.
2. Methods

2.1 Sample characterization

The natural sample used in this study is from the type locality Reed Station, Tiburon Peninsula, Marin Co., California, USA [Ransome, 1895]. We characterized the sample with single-crystal diffraction and Raman spectroscopy, which both agree well with previous studies [Baur, 1978; Daniel et al., 2000; Meyer et al., 2001; Pawley and Allan, 2001]. Ambient pressure measurements were conducted on Beamline 11.3.1 at the Advanced Light Source (ALS) at Lawrence Berkeley National Lab in Berkeley, CA.

2.2 High-pressure single crystal diffraction

High-pressure single-crystal measurements were carried out using either a Merrill-Bassett (HPDO) or BX90 (DESY) type diamond anvil cell (DAC) equipped with type Ia 500 μm culet Boehler-Almax [Boehler and De Hantsetters, 2004] geometry diamond anvils with 80° or 85° angular access. Rhenium gaskets with a 250 μm hole were used to contain the samples. Single crystals of lawsonite and ruby were loaded into the sample compartment with a mixture of 4:1 methanol ethanol as the pressure medium. Methanol:ethanol mixtures remain hydrostatic up to ~10.5 GPa [Klotz et al., 2009]. The standard ruby fluorescence gauge was used to determine pressure [Mao et al., 1986].

High-pressure single-crystal X-ray diffraction measurements were conducted at Beamline 12.2.2 at the ALS. The DAC was mounted on a Huber sample stage, and shutterless single-crystal diffraction data were collected on a Perkin Elmer amorphous silicon detector using synchrotron radiation monochromated by silicon(111) to a wavelength of 0.49592(2) Å (25 keV). Distance and wavelength calibrations were done using a NIST single crystal ruby
diffraction standard. Phi scans were employed to measure across both diamonds with 0.25° image width.

2.3 Data processing

Image masks, to avoid integrating signal from detector regions obscured by the DAC, were created using the program ECLIPSE [Parsons, 2010]. The data were integrated using the program SAINT v8.34A. A multi-scan correction for absorption was applied using the program SADABS-2014/11. Structures were solved by dual space methods (SHELXS-97/ SHELXT) and refined by full-matrix least-squares on $F^2$ (SHELXL-2014) [Sheldrick, 2008] using the graphical user interface ShelXle (Hubschle et al. 2011). Crystallographic parameters for our structure refinements are shown in Table 1. All atoms in the room pressure structure were refined anisotropically except for the hydrogen atoms, and in the high-pressure structures only the metals were refined anisotropically. For the high-pressure structures, we fixed the O-H bond lengths for the hydroxyls at 0.90(2) Å and for the H$_2$O molecule, we fixed the O-H bond length to 0.93(2) Å and the H-H distance to 1.5(4) Å. We chose these OH bond lengths based on reported single-crystal neutron diffraction study [Kolesov et al., 2008]. We also set the thermal parameters of the H atoms to ride on their respective oxygen atoms. Complete crystallographic information files (CIFs) for each structure can be found in supplementary material, as well as a discussion on the selection of our unit cells. A detailed discussion of our unit cell selection as well as our atom naming convention can be found in supplementary material.

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<td>orthorhombic Cmcm</td>
<td>orthorhombic Cmcm</td>
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Table 1. Crystal structure refinement information for orthorhombic and monoclinic lawsonite on compression. Complete CIFs are found in supplementary material.

3. Results and Discussion

3.1 Unit cell under compression

We collected diffraction patterns at various pressures up to ~10 GPa. The reflections can be indexed to an orthorhombic C unit cell up to ~9.3 GPa. Starting at pressures of ~8.4 GPa, we did observe weak reflections that are systematically absent in a C-centered orthorhombic unit cell (e.g. (017)) this is notably in excess of the pressure of onset (4 GPa) of such forbidden reflections reported by Boffa Ballaran and Angel (2003). However, all other observed reflections could be indexed to an orthorhombic C unit cell. These weak reflections did not grow in intensity under compression from ~8.4 to 9.3 GPa. All attempts to index the reflections collected between ~8.4 GPa and ~9.3 GPa to an orthorhombic P-centered unit cell failed. The structure of lawsonite was solved at 5.3, 8.4, 9.3, and 9.7 GPa. We index the reflections collected at 5.3, 8.4, and 9.3 GPa to an orthorhombic C unit cell, and we determined the spacegroup to be $Cmcm$. We index the reflections collected at 9.7 GPa to a monoclinic P unit cell, and determined the spacegroup to be $P2_1/m$ (Table 1). The symmetry we determined for the high-pressure phase is in accord with that inferred from analysis of high-pressure
polycrystalline data by Pawley and Allan (2001).

3.2 H$_2$O molecule

In orthorhombic Cmcm lawsonite, the H$_2$O molecule is H-bonded to the O4 oxygens (Figure 2a) and the H atoms are dynamically disordered between two equivalent sites [Libowitzky and Armbruster, 1995; Libowitzky, 2009]. Our single-crystal data show that the donor-acceptor distances in orthorhombic lawsonite between O5 and O4 decrease symmetrically by ~0.7 Å by 9.3 GPa, and that these oxygens lie in the same plane with the two H atoms associated with the water. This is in contrast to the changes observed at low temperature, where the distance between O5 and the two O4 atoms decrease by different amounts and the position of the H$_2$O molecule is refined as being oriented towards the closest acceptor: O4 [Libowitzky and Armbruster, 1995]. The decrease in distance of this hydrogen-bonded unit associated with the water molecule that is observed under compression is significant, and the H-bonds of the H$_2$O molecule are strengthened, which stabilizes its configuration. Since the two H-bond distances decrease by the same amount, the H$_2$O molecule is not expected to rotate or “freeze” into an ordered position. The cross channel distances between O4-O4 and O2-O2 change by essentially the same amount (~0.13 Å) from ambient to 9.3 GPa, whereas the O3-O3 distance only changes by ~0.03 Å. This indicates that the channel dimensions are not compressing isotropically. As the channel dimensions relative to the O5 water atom change symmetrically, there is no evidence that suggests that the H$_2$O molecule orders under compression. Moreover, it likely remains dynamically disordered under compression to at least 9.3 GPa, and our refined position at 9.3 GPa is the average position of the H$_2$O molecule.
Figure 2. H$_2$O hydrogen-bonding environment of (a) orthorhombic lawsonite at 9.3 GPa, and (b) monoclinic lawsonite at 9.7 GPa. The H$_2$O molecule in monoclinic lawsonite rotates into the page, and rotation in the $ab$ plane is not observed. Dotted lines represent H-bonds of the H$_2$O molecule. Atom colors are the same as Figure 1.

Across the orthorhombic to monoclinic phase transition, the two oxygen atoms to which the H$_2$O molecule is H-bonded move out of the plane. This motion causes the H$_2$O molecule to rotate slightly in order to remain H-bonded to these closest acceptors (Figure 2b). For reference, the H$_2$O molecule in the isostructural mineral bartelkeite (PbFeGe$^{VI}$(Ge$_2^{IV}$O$_7$)(OH)$_2$·H$_2$O) shows the same change in orientation (Origlieri et al., 2012).

Importantly, the distances between O5 and the two O4 atoms change by the same amount, demonstrating that neither acceptor becomes closer across the transition, and hence the H$_2$O molecule remains symmetrically oriented, and disordered. The H-bonding environment of the H$_2$O molecule does become more complex in monoclinic lawsonite (Figure 2a). This is due to O2 splitting into the separate sites O2A and O2B, which creates two different, longer donor-acceptor lengths from the O5 water atom to O2A and O2B in monoclinic lawsonite. At 9.7 GPa, these two oxygen atoms are still far enough away (>3.0 Å), that they are expected to only form weak (if any) hydrogen bonds.
Thus, our single-crystal data do not provide any evidence that the H$_2$O molecule becomes ordered in monoclinic lawsonite. Our refined H$_2$O position in monoclinic lawsonite is therefore likely an average position of the H$_2$O molecule. A modest shift in orientation, but not ordering, is consistent with previous Raman and infrared spectroscopic investigations which indicate that the H-bonding environment of the H$_2$O molecule does not change significantly under compression or across the orthorhombic to monoclinic phase transition (Scott and Williams 1999; Daniel et al. 2000). Moreover, ordering of the H$_2$O molecule in lawsonite across its low-temperature phase transitions produces a discrete H-bonding environment for the H$_2$O molecule, which is spectroscopically manifested by a decrease in the FWHM of the O-H vibrational modes [Kolesov et al., 2008; Libowitzky, 2009]. Decreases in the FWHM of the O-H vibrational modes under compression is not observed, suggesting that the H$_2$O molecule does not order under compression to at least 20 GPa [Scott and Williams, 1999; Daniel et al., 2000; Scott et al., 2007].

3.3 Hydroxyls

The hydroxyls in room temperature orthorhombic Cmcm lawsonite are also disordered [Libowitzky and Armbruster, 1995; Libowitzky, 2009]. In orthorhombic Cmcm lawsonite, the hydroxyls are located on the O4 oxygens in the small channel (Figure 1) and the hydroxyl is H-bonded to two symmetrically equivalent O2 atoms (Figure 3a). At 9.3 GPa, the O4 to O2 distance is 2.853(3) Å, and the hydrogen-bond angle between O4-H···O2 is ~132°. Interestingly, the cross channel distance (O4 to O4) and the O4 to O5 distances are both shorter (2.575 and 2.671 Å, respectively) than the O4 to O2 distance. The hydrogen bond might be expected to be oriented towards the closest acceptor, which in lawsonite at room pressure and temperature is...
the O4 atom. However, H-H repulsion between the hydroxyls likely prevents them from being oriented/hydrogen-bound out into the small channel at the same time, or flipping towards the O5 oxygen (assuming that the orientation of the H2O molecule does not change). At 9.3 GPa, the configuration of the hydroxyls changes slightly from ambient pressures, and our refined positions place the hydroxyl H-atoms out into the small channel. Since this is an average position for the hydroxyl H-atoms, this shift indicates that the H-bonding across the small channel has increased under compression to 9.3 GPa. This change is consistent with the hydroxyls becoming more delocalized, and hence more disordered: the shift of hydroxyls into the channel is not surprising since the cross-channel distance decreases by ~0.13 Å to 9.3 GPa, and this behavior may be precursory to the high-pressure phase transition. The refined H-H distance at 9.3 GPa is too close (at ~1.09 Å), and there may be cooperative motion between the hydroxyl units, with both being unlikely to be H-bonded out in the channel simultaneously due to H-H repulsion.
Figure 3. Hydroxyl H-bonding environment of (a) orthorhombic lawsonite at 9.3 GPa, and (b) monoclinic lawsonite at 9.7 GPa. Note that the hydroxyls in monoclinic lawsonite re-orient towards the closest acceptor (O2B). Dotted lines indicate H-Bonds and dashed lines are distance between hydroxyl oxygen and O2 or O2A or B. Atom colors are the same as Figure 1, in panel (b) Al1b is shown in light pink (top octahedral site).

In the high-pressure monoclinic phase, O2\text{orth} splits into O2\text{A}_{\text{mono}} and O2\text{B}_{\text{mono}} [Pawley and Allan, 2001; Liebscher et al., 2010] which gives rise to two different donor-acceptor distances from O4 to O2A and O2B (Figure 3b). At 9.7 GPa, the donor-acceptor distance from O4 to O2A and O2B is 2.917(11) Å and 2.733(38) Å respectively. The hydroxyl is observed to reorient towards the O2B atom (Figure 3b), and the angle between O5-H⋯O2B is ~148°, while between O5-H⋯O2A, it is ~118°. It should be noted that these unusual hydrogen bond angles are strongly indicative of dynamic disorder [Brown, 1976]. This re-orientation minimizes the H-
H repulsion between the two H-atoms of the hydroxyls that reside in the same channel. The observed orientation of the hydroxyls in monoclinic lawsonite is similar to that observed in the Pb-Ge lawsonite-like monoclinic phase bartelkeite. In bartelkeite, the hydroxyls are oriented towards the closer acceptor O2B and engaged in one strong H-bond and one weak H-Bond [Origlieri et al., 2012]. As in orthorhombic lawsonite, H-H repulsion in monoclinic lawsonite likely prevents the re-orientation of both hydroxyls out into the channel, and H-H repulsion likely increases under compression to ~9.3 GPa.

As with the H2O molecule, our single-crystal data provide no evidence that hydroxyls become ordered in monoclinic lawsonite. From a vibrational spectroscopic perspective, changes in the H-bonding environment of the hydroxyls are the primary manifestation of the orthorhombic to monoclinic phase transition (e.g. Scott and Williams, 1999; Daniel et al., 2000; Scott et al., 2007). Scott and Williams (1999) report that the pressure shifts of both of the infrared hydroxyl stretching vibrations change near 9.0 GPa, with one of them beginning to shift negatively above ~9.0 GPa. Their interpretation was that changes in O-O distances primarily control the behavior of the hydroxyls in orthorhombic lawsonite, whereas changes in O-H···O angles primarily control the behavior of the hydroxyls in monoclinic lawsonite. For comparison, the Raman active OH stretching modes initially shift positively, but also shift negatively on the transition to the high-pressure phase of lawsonite (Daniel et al. 2000). High-pressure far infrared spectra show that a new band near 368 cm⁻¹ appears in the monoclinic phase of lawsonite, which is likely produced by librational motion of the OH groups and indicates that the OH environment changes in monoclinic lawsonite [Scott et al., 2007]. Thus, previous spectroscopic investigations are in full accord with our single-crystal refinement in showing that
the H-bonding environment of the hydroxyls becomes more complex in monoclinic lawsonite. Indeed, our single crystal structural refinement of monoclinic lawsonite show that the hydroxyls re-orient in monoclinic lawsonite, and that the disordered hydroxyl positions in monoclinic lawsonite include displacements along the c-axis of the crystal structure.

4. Mechanism of high-pressure phase transition

Previously the phase transition mechanism was described as a shearing of the structure that opens up the monoclinic β angle (Daniel et al. 2000, Pawley and Allan 2001). Daniel et al. (2000) propose that the phase transition is ferroelastic in nature, and that it is driven by shear. Pawley and Allan (2001) state that shearing parallel to the AlO$_6$ octahedral chains breaks the symmetry of the Al-O2-Si angles, doubles their numbers, and opens up the monoclinic β angle.

Our data indicate that the orthorhombic to monoclinic phase transition between 9.3 and 9.7 GPa is neither driven by a change in coordination number of the Ca cation nor by a noticeable shearing of the structural framework. Instead, it is driven by an instability of the O1 atom due to an increase in compressional strain (overbonding) of O1.

Here we use the bond valence model [Brown, 2002] to quantitatively analyze the lawsonite high-pressure phase transition. In this model, bond valences describe the strength of a bond and are uniquely related to bond lengths through the relationship

\[ S_{ij} = \exp(R_0 - R_{ij}/b) \]  

(1)

with $S_{ij}$ representing the bond valence between atoms i and j, $R_{ij}$ the respective bond length and $R_0$ and b empirically determined atom-pair specific constants. For a given bond topology (i.e. the connectivity of the cations and anions in the compound), each bond has a unique bond valence (and thus bond length) defined by the two network equations:
\[ V_i = \sum_j S_{ij} \]  
\text{(2) Valence sum rule}

\[ 0 = \sum_{\text{loop}} S_{ij} \]  
\text{(3) Equal valence rule}

Equation 2 states that the sum of all bond valences converging on any cation or anion is equal to the absolute value of the atom’s valence. Equation 3 requires the sum of all bond valences along any given topologic loop in the structure to be zero, assuming bond valences to be positive when looping from cation to anion, and negative when moving within the loop from anion to cation. This equation formalizes the requirement that bond valences should be distributed with the highest possible symmetry around any atom (Pauling’s principle of parsimony Pauling, 1929). The network equations predict bond valences and thus bond lengths based on the bond topology. Mapping a given bond topology into 3-dimensional space leads in a general case to conflicting requirements due to mismatched dimensions of unstrained structural units. Therefore, comparing the bond valences predicted by the network equations with actually observed bond valences helps to understand where a given structure is strained due to steric mismatches and what limits its stability and thus drives observed phase transitions. The main conclusions of this analysis are that the observed details of the Lawsonite structure and its phase transition are controlled by the size mismatch of the Ca cation and its site on the one hand and the intrinsic overbonding of the bridging oxygen O1 on the other hand (Figure 5). A more detailed discussion can be found in the supplementary material.

The pressure evolution of the Ca-O bonds (Figure 4) is observed within a group of fairly strong \( s_{ij} > 0.2 \text{ v.u.} \) bonds (Ca-O1, Ca-O2, Ca-O5). In this group, the Ca-O bonds linked to the aluminosilicate framework show a general strengthening trend while O5, linked only to Ca and
the H$_2$O molecule stays more or less constant in strength. Across the phase transition, the Ca-O1 bonds strengthen only slightly, while the 4 Ca-O2 bonds weaken. These 6 Ca-O bonds are clearly differ in strength from the Ca-O3 bond which is not only much weaker ($s_{ij} < 0.1$) than Ca-O1, Ca-O2 and Ca-O5 but also does not change significantly with increasing pressure up to and across the phase transition. Therefore, there is no physical rationale to propose anything other than 6-fold coordination for Ca at all pressures probed, and across the phase transition. The Ca site also becomes markedly distorted across the transition, see supplementary Table S1 for the calculated distortion parameters for the Si, Al and Ca sites in lawsonite as a function of pressure. The general topology of the lawsonite structure remains unchanged across the phase transition. Indeed, when comparing the orthorhombic and monoclinic structures, it is visually difficult to discern any difference (Figure S1). At 9.3 GPa, the angle of what will become the monoclinic $\beta$-angle in the orthorhombic structure is 123.66°: this changes to only 124.47° across the phase transition. The largest atomic shifts from 9.3 to 9.7 GPa are observed for O1 and O5 (Table 2). Their shift vectors are almost parallel (angle $\sim 1.6^\circ$) and lie in the monoclinic $a$-$c$ plane.
Figure 4. Bond valences and their evolution with pressure for the Ca-O bonds. Note the clustering of the O1, O2 and O5 bonds around 0.25 v.u. while O3 is separated from this group with values below 0.08 v.u. There is also a lack of any significant change of the Ca-O3 bond with increasing pressure. This strongly suggests that the Ca in lawsonite remains 6 coordinated up and across its phase transition between 9.3 and 9.7 GPa.

<table>
<thead>
<tr>
<th></th>
<th>9.3 GPa Ortho-MonoSetting</th>
<th>9.7 GPa Mono</th>
<th>Shift (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca</td>
<td>0.3374 0.75 0.6687</td>
<td>0.3386 0.75 0.6795</td>
<td>0.058</td>
</tr>
<tr>
<td>Al1A</td>
<td>0.5 0 0.5</td>
<td>0.5 0 0.5</td>
<td>0</td>
</tr>
<tr>
<td>Al1B</td>
<td>0.5 0 0</td>
<td>0.5 0 0</td>
<td>0</td>
</tr>
<tr>
<td>Si</td>
<td>-0.0410 0.1335 0.9795</td>
<td>-0.0377 0.1342 0.9866</td>
<td>0.035</td>
</tr>
<tr>
<td>O1</td>
<td>0.8920 0.75 0.946</td>
<td>0.8885 0.75 0.9150</td>
<td>0.167</td>
</tr>
<tr>
<td>O2A</td>
<td>0.7514 0.1191 0.6452</td>
<td>0.7525 0.1211 0.6488</td>
<td>0.031</td>
</tr>
</tbody>
</table>
Table 2: Comparison of atomic shifts across the phase transition between 9.3 and 9.7 GPa. The orthorhombic coordinates at 9.3 GPa were transformed into the monoclinic reference system using the transformation matrix 

\[
\begin{bmatrix}
0 & 2 & 0 \\
0 & 0 & 1 \\
1 & 1 & 0
\end{bmatrix}
\]

The shift was calculated using the monoclinic 9.7 GPa cell parameters.

The lawsonite structure exhibits a peculiar pattern of internal strains at ambient conditions. This is plotted together with its pressure evolution in Figure 5 as a relative deviation of the bond valence sum from the ideal value. Disregarding the less-well-determined O-H bonds linked to O4 and O5, we find a tensional strain (underbonding) for Ca, O2 and O3 and high compressional strain (overbonding) for O1. Si and Al are well within the ‘comfort zone’ of ± 5 % deviation from ideal bonding. The overall tensile strain in the lawsonite structure at ambient pressure is not surprising given that it is a mineral stabilized at high pressure. The peculiar situation of O1 can be understood in terms of its role as the bridging oxygen in the Si$_2$O$_7$ group. Being coordinated to two Si atoms with ideal bond valences of 1.0 v.u. for each bond, saturates the bond valence requirements of O1 (i.e. 2.0). Its additional somewhat forced coordination to Ca leads to the observed overbonding. The application of pressure moves the underbonded atoms into the ideal bonding comfort zone while the overbonding of O1 becomes more pronounced. Finally at 9.3 GPa, O1 is overbonded by 20%, which is often viewed as the limit for structural stability [Brown, 2002]. At this pressure all cations are slightly overbonded as well. We regard the massive overbonding of O1 as the driving force of the ensuing phase transition between 9.3 and 9.7 GPa, particularly as the phase transition leads to a substantial decrease in
the overbonding of O1. Hence, the O1 atom plays the villain in the high-pressure orthorhombic to monoclinic phase transition.

Figure 5. Relative deviation of observed bond valence sums ($S_{ij}$) from their ideal values (i.e. absolute values of atomic valence ($V_i$)). The grey shaded area is regarded as a “comfort zone” for the internal strain in an extended crystal structure.

The reduction of overbonding is mainly achieved by a slight lengthening (i.e. weakening) of the two O1-Si bonds at the O1 atom. In order to achieve this, O1 moves off the mirror/glide planes, which reduces the point group symmetry from 2/m 2/m 2/m to 2/m, and hence the orthorhombic to monoclinic phase transition occurs. The shift of O1 away from the orthorhombic c-glide plane is by approximately 0.24 Å roughly parallel to the $b$-axis. This shift of the Si$_2$O$_7$ bridging oxygen leads to a slight rotation of the rigid SiO$_4$ tetrahedra, which in turn leads to a twisting of the octahedral chain, to which they are attached, away from a straight
edge-connected chain (Figure 6). This twisting leads to a splitting of both, the Al cation and O2 anion through the loss of C centering. Nevertheless, the individual atomic shifts are quite small (Table 2). Thus, the net effect of the phase transition is to remove a topologically-induced overbonding via a relatively modest deformation, and it is this deformation that likely allows the monoclinic lawsonite phase to be stable at pressures above ~9.5 GPa.

Figure 6. Illustration of the O1 shift off the mirror/glide planes. The plane defined by Si-O1 and O3 at the two SiO$_4$ tetrahedra tilts at O1 by an angle of ~9°. The shift in distances of the individual atoms are given in Table 2.

5. Geophysical Implications

Notably, lawsonite has been observed to be stable to pressures as high as 14 GPa at temperatures of ~600°C, which represent conditions encountered in cold subduction environments [Pawley, 1994]. Our results have implications for the anisotropy, crystal structure, and phase transitions of lawsonite as it is subducted to depth within meta-basalts in Earth’s mantle. In particular, lawsonite compresses nearly isotropically up to the ~9.3 GPa phase transition, confirming previous inferences from polycrystalline diffraction (Im and Lee,
2016): thus, the level of compressional wave anisotropy in lawsonite is likely to remain relatively constant under compression [Boffa Ballaran and Angel, 2003; Fujimoto et al., 2010; Chantel et al., 2012]. We do not observe a previously reported transition from orthorhombic C to orthorhombic P symmetry near 4.0 GPa, nor at pressures higher than 4.0 GPa, and lawsonite undergoes only one phase transition, from orthorhombic to monoclinic symmetry near 9.5 GPa, under compression to ~10.0 GPa.

Across the transition, the Ca site becomes markedly distorted (Table S1), O2 splits into two separate oxygen sites, O2A and O2B, and Al1 splits into two octahedral sites, Al1A and Al1B, and the disordered hydroxyls become more delocalized, and their distribution shifts along the c-axis. The shifts in distortion, numbers of sites, and increased delocalization documented here each imply that monoclinic lawsonite is a higher entropy phase than orthorhombic lawsonite (e.g. $\Delta S_{\text{ortho-mono}}$ is positive), which is consistent with a previous inference of Liebscher et al. (2010) based on the Sr-analogue of lawsonite. Pawley and Allan (2001) proposed a positive Clapeyron slope for this transition (and hence lower entropy for the high pressure phase), but ultimately concluded that “a negative slope cannot be ruled out.” Our structural solutions of the high-pressure phase show that the volume change $\Delta V_{\text{ortho-mono}}$ is small and negative, consistent with previous studies of Daniel et al. (2000), Pawley and Allan (2001), and Boffa Ballaran and Angel (2003).

Hence, monoclinic lawsonite is expected to occur at lower pressures than its ~9.5 GPa pressure of occurrence at 300 K, within warmer subduction zone environments. Given the expectation that the $Cmcm$-$P2_{1}/m$ transition has a negative slope, the high-pressure monoclinic phase of lawsonite is expected to exist in meta-basalt assemblages in cold subduction.
environments approaching and exceeding 300 km in depth, barring any undocumented high-
temperature polymorphism. Notably, the stability field of lawsonite in the CASH system was
determined from the analysis of high-pressure run products (e.g., Schmidt and Poli, 1994), and
the phase of lawsonite in situ in these experiments is not known. Even if the Clapeyron slope of
the transition is close to flat, there is still a large pressure and temperature range where
monoclinic lawsonite would be stable within cold subduction environments (Figure 7). Hence,
we expect that this modestly distorted form of lawsonite is a major carrier of water to depths
approaching the transition zone, and is of key importance in transporting water into the deep
upper mantle.
Figure 7. Possible slopes for the Cmcm to P21/m phase transition. The negative slope is constrained by the grey region. Grey region represents the stability field of Cmcm lawsonite determined in situ [Comodi and Zanazzi, 1996; Pawley et al., 1996; Chinnery et al., 2000; Grevel and Nowlan, 2000; Pawley and Allan, 2001]. The positive slope is constrained by data from Pawley and Allan (2001). The arrow with the question mark represents the P & T regime that the phase transition could occur based on all the available data. Hypothetical slab pressure-temperature paths from [Ono, 1998]. Lawsonite stability in CASH system, solid black line [Newton and Kennedy, 1963; Pawley, 1994; Schmidt and Poli, 1994]. Figure modified after Liebscher et al. (2010).

The distorted Ca site and multiple Al-sites of monoclinic laswonite also have implications for the geochemical partitioning behavior of elements at depth and during dehydration.

Halogen partitioning in subducting slabs is complex, and lawsonite does incorporate trace amounts of F, Cl, Br, and I [Pagé et al., 2016]. Indeed, upon apatite decomposition at ~200 km, F has been proposed to be sequestered in lawsonite and phengite [Pagé et al., 2016]. Thus, lawsonite and phengite represent two of the few minerals that may transport F to depths greater than 200 km. The increased H-H repulsion in the monoclinic phase of lawsonite raises the energy associated with the hydroxyl substitution, which could increase the solubility of F in monoclinic lawsonite. This H-H repulsion could lead to destabilization of monoclinic lawsonite at high-pressures and temperatures. Hence, F substitution into monoclinic lawsonite would likely stabilize this structure since it would remove the H-H repulsion [Williams 1992].

Speculatively, monoclinic lawsonite may, within cold subduction zones, be a significant means of transport of F to depth, which could contribute to the high F content observed in deep mantle, subduction-associated magmas [Paul et al., 1976; Kendrick et al., 2015]. Ultimately, if the transition zone functions as an F repository (e.g., Roberge et al., 2015), monoclinic lawsonite could be a primary mechanism through which F is transported to depths close to this region of the planet.
The monoclinic phase is anticipated to impact lawsonite stability and the manner in which lawsonite dehydrates in subduction zones. Our single crystal structure shows that the H-bonding environment of the H$_2$O molecule changes across the transition in a manner that stabilizes the average position of the molecule across the transition. With respect to the hydroxyls, they re-orient slightly towards the closer acceptor (O2B), which changes their average position along the c-axis. This, combined with the rotation of the H$_2$O molecule in the ± c-direction, suggests that the electrical conductivity via proton mobility of the monoclinic phase may be enhanced along the c-direction. It should be noted that the strength of H-bonding the monoclinic lawsonite increases as pressure increases [Scott and Williams, 1999; Daniel et al., 2000]. However, an increase in proton delocalization would likely dominate over the increase in H-bonding strength which would result in an increase in electrical conductivity. Our single crystal data provides the first evidence of reorientations of the H$_2$O molecules and hydroxyls across the orthorhombic to monoclinic lawsonite phase transition. These re-orientations could also be relevant to the detailed dehydration mechanism of lawsonite, which is currently poorly understood. The actual mechanism of lawsonite dehydration is important, since it has been suggested that lawsonite dehydration could directly trigger earthquakes in subducting oceanic crust [Okazaki and Hirth, 2016; Incel et al., 2017]. The relative bonding environments of the water molecules and hydroxyl units indicate that the dehydration of monoclinic lawsonite could be a multi-stage process that commences with the hydroxyls, as they are both significantly more disordered in monoclinic lawsonite, and in relatively close proximity to one another. Hence, relative to the stabilized position of the water molecule in the monoclinic phase, the hydroxyl units may be more prone to being destabilized within monoclinic lawsonite.
Acknowledgements

We acknowledge A. Pawley for helpful comments which improved the quality of this manuscript. We thank S. Teat for experimental help with the ambient single crystal measurements on beamline 11.3.1. Work partially supported by NSF through EAR-1215745 and -1620423, and COMPRES under NSF Cooperative Agreement EAR 11-57758. The Advanced Light Source is supported by the Director, Office of Science, Office of Basic Energy Sciences, of the U.S. Department of Energy under Contract No. DE-AC02-05CH11231. All data for this manuscript can be found in the manuscript or the supplementary material.

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