

First-principles investigations of the polysomatism of antigorite under pressure

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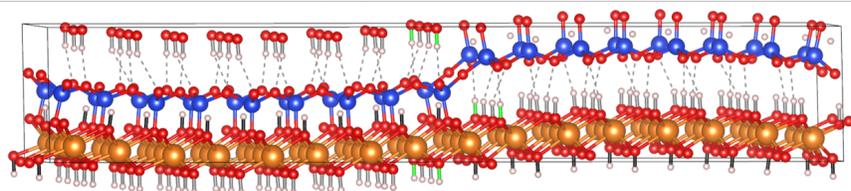
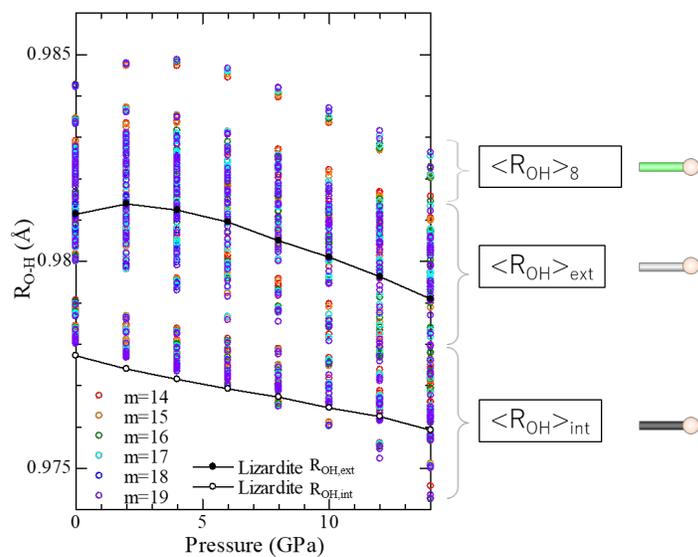
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October 27, 2023

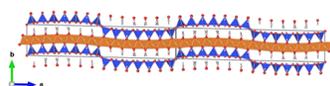
Abstract

Antigorite is the high-temperature member of the serpentine group minerals and is broadly considered a primary carrier of water in subducting oceanic lithosphere at the fore-arc. It has a wavy crystal structure along the a-axis and several polysomes with different m -values ($m=13-24$) have been identified in nature. The number (m) is defined as the number of tetrahedra in one wavelength and is controlled by the misfit between the octahedral and tetrahedral layers. The degree of misfit mainly depends on the volumes of the MgO₆ octahedra and SiO₄ tetrahedra within the layers, which vary as a function of temperature and pressure. However, it is not well understood which m -values of antigorite are stable at different temperature and pressure conditions. To investigate the pressure dependence of the stability of different m -values in antigorite, we performed first-principles calculations for several polysomes ($m=14-19$) at high pressure (0-14 GPa) and compared their enthalpies (T: static 0 K). We found that although the energy differences between polysomes are small, polysomes with larger m -values are more stable at ambient pressure, while polysomes with smaller m -values are more stable at elevated pressures. This suggests that the structure of antigorite in oceanic lithosphere that has subducted into the deep Earth may gradually evolve into a different polysome structure than antigorite samples observed at ambient or near-pressure conditions. This structural change may be related to the formation of the lower plane of the double seismic zone, as changes in polysome m -values are accompanied by a minor dehydration reaction.

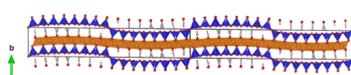


m:even: space group $C2/m$

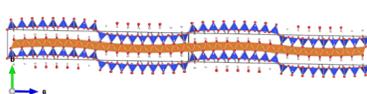
$m=14 Mg_{39}Si_{28}O_{70}(OH)_{50}$ $N_{atom}: 237$



$m=16 Mg_{45}Si_{32}O_{80}(OH)_{58}$ $N_{atom}: 273$

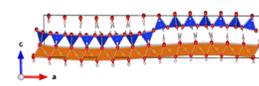


$m=18 Mg_{51}Si_{36}O_{90}(OH)_{66}$ $N_{atom}: 309$

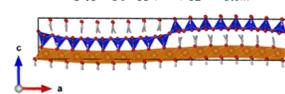


m:odd: space group Pm

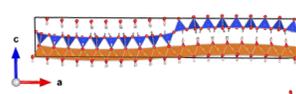
$m=15 Mg_{42}Si_{30}O_{75}(OH)_{54}$ $N_{atom}: 255$

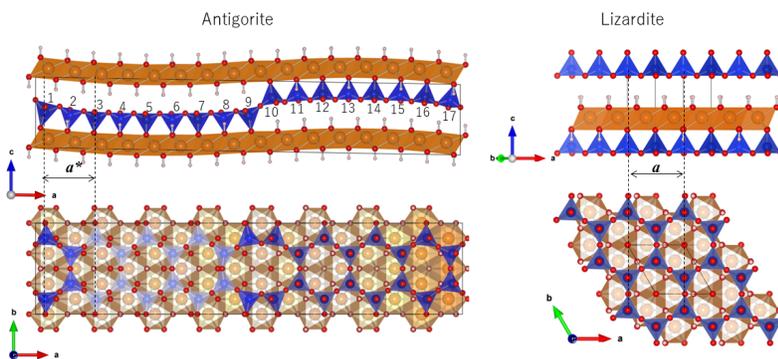
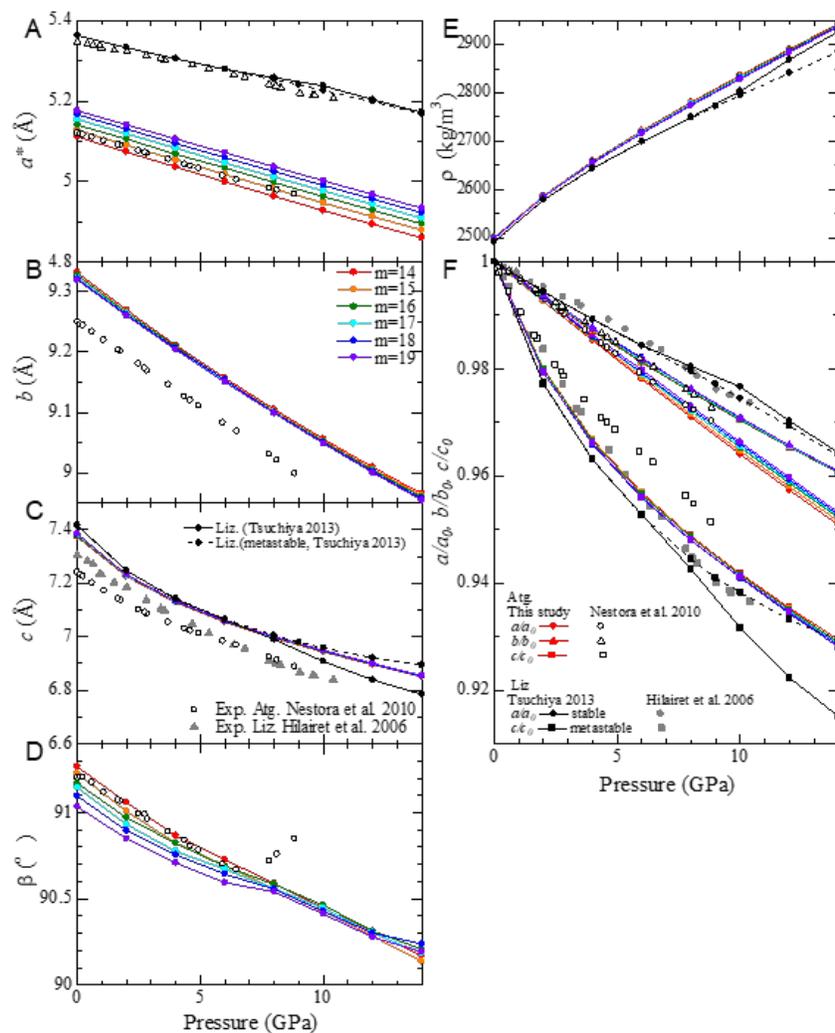


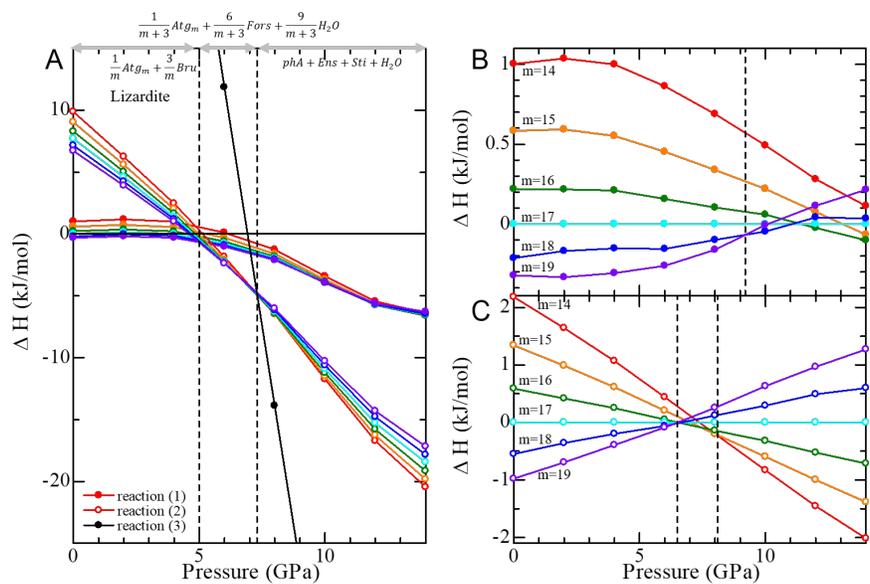
$m=17 Mg_{48}Si_{34}O_{85}(OH)_{62}$ $N_{atom}: 291$



$m=19 Mg_{54}Si_{38}O_{95}(OH)_{70}$ $N_{atom}: 327$







1 **First-principles investigations of the polysomatism of**
2 **antigorite under pressure**

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6 **Key Points:**

- 7 • Antigorite crystal structures with various ($m = 14-19$) were determined by first-
8 principles calculation under pressure.
9 • The relative enthalpy shows that antigorite with smaller m -values are stabilized
10 with increased pressure.
11 • Antigorite in subducting slabs may gradually dehydrate under high pressure as a
12 result of changes to stable m -values.

Abstract

Antigorite is the high-temperature member of the serpentine group minerals and is broadly considered a primary carrier of water in subducting oceanic lithosphere at the fore-arc. It has a wavy crystal structure along the a -axis and several polysomes with different m -values ($m=13-24$) have been identified in nature. The number (m) is defined as the number of tetrahedra in one wavelength and is controlled by the misfit between the octahedral and tetrahedral layers. The degree of misfit mainly depends on the volumes of the MgO_6 octahedra and SiO_4 tetrahedra within the layers, which vary as a function of temperature and pressure. However, it is not well understood which m -values of antigorite are stable at different temperature and pressure conditions. To investigate the pressure dependence of the stability of different m -values in antigorite, we performed first-principles calculations for several polysomes ($m=14-19$) at high pressure (0-14 GPa) and compared their enthalpies (T: static 0 K). We found that although the energy differences between polysomes are small, polysomes with larger m -values are more stable at ambient pressure, while polysomes with smaller m -values are more stable at elevated pressures. This suggests that the structure of antigorite in oceanic lithosphere that has subducted into the deep Earth may gradually evolve into a different polysome structure than antigorite samples observed at ambient or near-pressure conditions. This structural change may be related to the formation of the lower plane of the double seismic zone, as changes in polysome m -values are accompanied by a minor dehydration reaction.

Plain Language Summary

Antigorite is a hydrous mineral that is believed to be an important carrier for transporting water into the Earth's interior. However, its crystal structure is very complex, and it is not well understood which structural variant is stable at the high temperature and pressure conditions of the Earth's interior. In this study, several crystal structures of antigorite were calculated by first-principles calculations, and their enthalpies were compared to determine the stable structure as a function of pressure. The results indicate that the structure and chemical composition of antigorite may change under high pressure, resulting in the gradual release of water. This behavior may explain the cause of deep-focus earthquakes reported in the deep Earth.

1 Introduction

Serpentinite is a hydrous, ultramafic metamorphic rock composed of one or more of the serpentine subgroup minerals (antigorite, lizardite, chrysotile), and is broadly considered the primary carrier of water in subducting oceanic lithosphere at forearcs. These serpentine subgroup minerals share the nominal formula $\text{D}_3[\text{Si}_2\text{O}_5](\text{OH})_4$, in which $\text{D} = \text{Mg}$ with minor substitution of Fe, Ni, Mn, Al, or Zn. These minerals are both common and hydrous, as they form by the hydrothermal metamorphism of mafic or ultramafic rocks in the oceanic lithosphere and mantle wedge through the process of serpentinization (Guillot & Hattori, 2013). Serpentinization also functions as a lubricant for subducting slabs, promoting aseismic slip due to the rheological weakness of serpentinite (Hilairet et al., 2007; Hirth & Guillot, 2007). Additionally, serpentinite is the primary carrier of water in subducting oceanic lithosphere and can transport water in a subducting cold plate to a depth of ~ 200 km (e.g. Schmidt & Poli, 1998; Iwamori, 1998). Moreover, water released by the decomposition of serpentine minerals triggers magma generation in the mantle wedge above the subducting plate and is linked to island arc magmatism (Green, 2013; Tatsumi, 1986).

The stability and dehydration of serpentine minerals has also been extensively investigated in connection to intermediate and deep-focus earthquakes (e.g. (Peacock, 1990; Irifune et al., 1996; Omori et al., 2004; Komabayashi et al., 2005)). In particular, serpentine decomposition is thought to be closely related to the lower side of the Wadati-

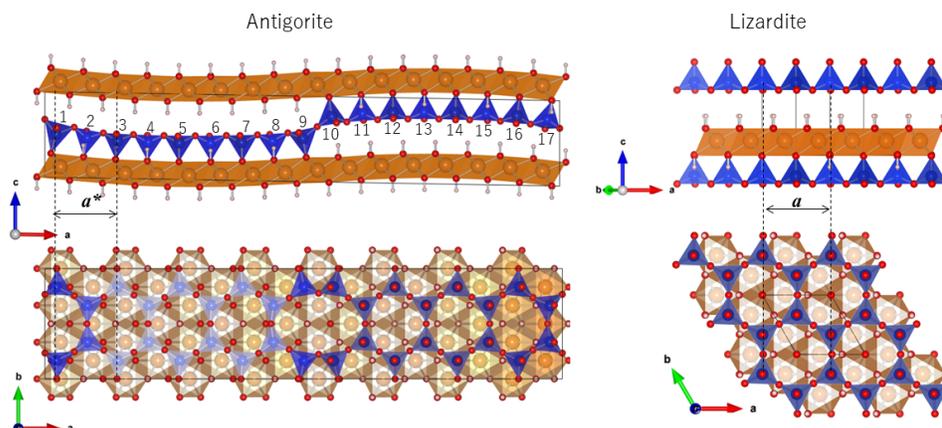


Figure 1. The structural differences between antigorite ($m=17$) and lizardite ($m=\infty$). a^* corresponds to the averaged length of two SiO_4 tetrahedra along a -axis of antigorite.

63 Benioff zone (Nishiyama, 1992; Kirby et al., 1996; Yamasaki & Seno, 2003). However,
 64 the pressure-temperature (P - T) conditions under which such deep-focus earthquakes
 65 occur are not a perfect match for the phase boundaries of serpentine minerals as deter-
 66 mined by laboratory experiments. Thus far, this discrepancy has been explained by the
 67 persistence of metastable serpentine in the subducting slab that eventually decomposes
 68 at sufficiently high P - T conditions (Peacock, 1990). Since the formation and decompo-
 69 sition of serpentine minerals are intrinsically linked to a wide range of subduction zones
 70 dynamics, it is important to determine the depth to which these hydrous phases are stable,
 71 motivating experimental and theoretical studies that synthesize and/or evaluate ser-
 72 pentine minerals at variable pressure and temperature conditions.

73 All three serpentine minerals (lizardite, chrysotile, and antigorite) are phyllosili-
 74 cates, with a 1:1 layer structure comprised of distinct layers of trioctahedral $\text{Mg}(\text{O},\text{OH})_6$
 75 and tetrahedral SiO_4 polyhedra, which are more broadly described as MO_6 and TO_4 sheets,
 76 respectively. However, even at ambient P - T conditions, there is a mismatch between
 77 the distance between the apical oxygen in the tetrahedral sheet (9.18 \AA) and the oxygen-
 78 oxygen distance in the brucite-like octahedral sheet (9.44 \AA) (Bailey, 1966). What dif-
 79 ferentiates the three serpentine minerals is how this $\sim 3\%$ discrepancy is resolved. In lizardite,
 80 which contains planar sheets of tetrahedral TO_4 and octahedral MO_6 , the difference is
 81 resolved via Al-substitution in the octahedral layer and very small grain sizes (Mellini,
 82 1982). In both chrysotile and antigorite, curvature is key, as the convex side of the TO_4
 83 sheet contains stretched oxygen-oxygen distances which can then match the concave (i.e.,
 84 compressed) side of an MO_6 sheet (Wicks & Whittaker, 1975). In chrysotile, the bend-
 85 ing of the sheets is continuous, resulting in nanotubes that give the mineral a fibrous habit,
 86 whereas in antigorite the structure is alternating wavy or corrugated with layers inter-
 87 connected and reversing the polarity of tetrahedral sheet at nodes along the a -axis (Fig-
 88 ure 1) (Wicks & O’Hanley, 1988).

89

90 There are several structural variations of antigorite which are defined by the m -
 91 value that corresponds to the number of TO_4 tetrahedra within a single wavelength along
 92 the a -axis. Typically, the tetrahedra form six-membered rings, as in most phyllosilicates.
 93 However, the orientations of the tetrahedra are reversed at the nodes or points of inver-
 94 sion of the wavy structure where bending is most extreme, leading to structures referred
 95 to as "8-reversals" and "6-reversals" (Capitani & Mellini, 2005). In 8-reversals, the tetra-
 96 hedra form the alternating 4- and 8-membered rings, where half of the convex of the tetra-
 97 hedra are facing up and the other half are facing down. In 6-reversals, the tetrahedra
 98 form the 6-membered rings with four facing up and two facing down along the $[010]$ di-
 99 rection. The 8-reversals and 6-reversals appear alternatively at the nodes of wavy struc-
 100 ture along the a -axis. According to Kunze, 1961, the chemical formula of antigorite is
 101 described as $\text{M}_{3m-3}\text{T}_{2m}\text{O}_{5m}(\text{OH})_{4m-6}$, where M is the octahedral site (M: Mg^{2+} , Fe^{2+} ,
 102 Al^{3+} etc.) and T is the tetrahedral sites (T: Si^{4+} , Al^{3+} , Fe^{3+} etc.). In natural samples,
 103 $m = 13 - 24$ have been identified, corresponding to $C_{H_2O} \simeq 12 - 12.5$ wt% (Mellini et
 104 al., 1987). Due to the link between polysomatism and chemical composition, antigorite
 105 is not a true polymorph of the other serpentine minerals, lizardite and chrysotile, due
 106 to its slight departure from the ideal $\text{D}_3[\text{Si}_2\text{O}_5](\text{OH})_4$ formula.

107 HRTEM studies have shown that antigorite with an m -value of 17 is the most abun-
 108 dant phase, and many studies have focused exclusively on this crystal polysome (Capitani
 109 & Mellini, 2007). Indeed, most first-principles calculations have been performed using
 110 the $m = 17$ antigorite polysome structure (Mookherjee & Capitani, 2011; Capitani &
 111 Stixrude, 2012; Ghaderi et al., 2015; Demichelis et al., 2016; Balan et al., 2021). Despite
 112 this assumption, TEM studies of hydrothermally synthesized antigorites at various tem-
 113 perature and pressure conditions show that the m -value changes as a function of pres-
 114 sure and temperature (Wunder et al., 2001; Shen et al., 2020). Smaller m -value means
 115 an increase in the number of Si-O bonds bridging the layers per unit volume. This may
 116 cause an increase in attractive interaction between layers and thus an increase in den-
 117 sity. Therefore, the phase diagram of antigorite which shows a decrease in m -value with
 118 increasing temperature is somewhat counter-intuitive. However, to date there has not
 119 been sufficient structural and thermodynamic corroboration regarding the stable polysome
 120 of antigorite at the P - T conditions of a subducting oceanic plate.

121 Importantly, while lizardite and chrysotile are stable at low temperatures (Evans,
 122 2004), antigorite only forms at elevated temperature ($>250^\circ\text{C}$) and has the highest ther-
 123 modynamic stability of the serpentine subgroup, increasing its importance as a host of
 124 hydrogen at increased depths. It has recently been suggested that polysomatism in the
 125 antigorite may be related to the reason why the deep seismicity at the lower surface of
 126 the Wadati-Benioff zone is not consistent with the phase boundary of the antigorite (Ferrant,
 127 2019). As the temperature and pressure dependence of antigorite polysomatism, i.e., the
 128 m -value, has not been solved, this study uses first-principles calculations to: (1) deter-
 129 mine structural models of antigorite with various m -values ($m = 14-19$), and (2) calcu-
 130 late the pressure dependence of their relative enthalpies. This method allows us to in-
 131 vestigate how the m -value, and therefore the chemical composition and dehydration, of
 132 antigorite varies as a function of pressure. The clarification of this behavior will make
 133 an important contribution to the understanding of the dehydration mechanism of ser-
 134 pentine in the deep Earth.

135 2 Methods

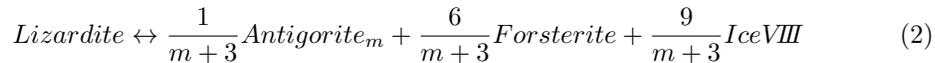
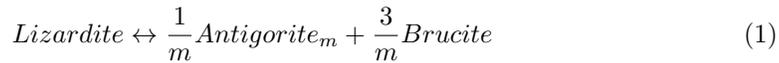
136 While density functional theory (DFT) (Hohenberg & Kohn, 1964; Kohn & Sham,
 137 1965) is exact for the energy and density of the electronic ground state, in practice it is
 138 necessary to employ approximations to describe the many-body effects involved in the
 139 exchange-correlation functional. Possible approximations include a local density approx-
 140 imation (LDA) or a generalized gradient approximation (GGA). A hydrogen bond is an
 141 electrostatic force induced between a weakly positive hydrogen atom due to the forma-

tion of a covalent bond with a highly electronegative atom and a surrounding electronegative atom. Chemical interactions in phyllosilicates, including antigorites, are the result of subtle competition between covalent, hydrogen bonding, and van der Waals interactions. Describing the complexity of these interactions continues to be a very challenging task. The computational results for systems involving hydrogen bonding are sensitive to the choice of an appropriate exchange-correlation functional (e.g., Hamann, 1997), as the local-density approximations (LDA) tend to overestimate hydrogen bonding and generalized gradient approximations (GGA), while a significant improvement, do not account for long-range electron correlation forces. In this study, our first-principles calculations utilize a generalized gradient approximation with a Perdew-Burke-Ernzerhof functional (GGA-PBE) (Perdew et al., 1996), as it allows for direct comparison with previous ab initio calculations of hydrous minerals, especially the lizardite study of Tsuchiya, 2013.

The Troullier-Martins type norm-conserving pseudopotentials (Troullier & Martins, 1991), which were extensively tested in previous calculations (e.g., Tsuchiya and Tsuchiya 2008, 2009) were used for Mg, Si and H atoms. The ultrasoft pseudopotential for oxygen atom was generated by the method of Vanderbilt (Vanderbilt, 1990). The electronic wave function was expanded in plane waves using a kinetic energy cutoff of 50 Ry. The crystal structures of antigorite with $m = 16$ (space group $C2/m$) and 17 (space group Pm) have been reported (Capitani & Mellini, 2004, 2006) based on single crystal X-ray diffraction experiments. In this study, we generated and relaxed antigorite polysome structures ($m=14-19$), where the space groups of odd and even m were set to Pm and $C2/m$, respectively (Fig. 2) (Capitani & Mellini, 2005).

The irreducible Brillouin zone of the antigorite primitive cell were sampled on $2 \times 2 \times 2$ ($m = 14, 16, 18$) and $1 \times 3 \times 3$ ($m = 15, 17, 19$) Monkhorst-Pack meshes. This sampling is particularly important for the calculation of enthalpies of even and odd m polysomes within comparable accuracy, as the primitive lattice vectors are totally different for the crystal structures of odd and even values of m (Uehara & Shirozu, 1985). In addition to the calculation of antigorites, we also calculated the enthalpies of lizardite, forsterite (Mg_2SiO_4), brucite ($Mg(OH)_2$), phase A ($Mg_7Si_2O_8(OH)_6$), clinoenstatite ($MgSiO_3$), stishovite (SiO_2) and ice VIII (H_2O). The k-point samplings are summarized in Table 1. In order to estimate the dehydration pressure of antigorite, k-points samplings were conducted at $3 \times 3 \times 2$ (phase A), $2 \times 2 \times 4$ (clinoenstatite), $6 \times 6 \times 6$ (ice-VIII) Monkhorst-Pack mesh. All structural parameters were fully relaxed at static 0 K using damped variable cell shape molecular dynamics using the quantum-espresso code (Giannozzi et al., 2009) until residual forces became less than 1.0×10^{-4} Ry/a.u.

In order to compare the enthalpies of antigorite with different m -values, the following chemical reactions were constructed with respect to lizardite:



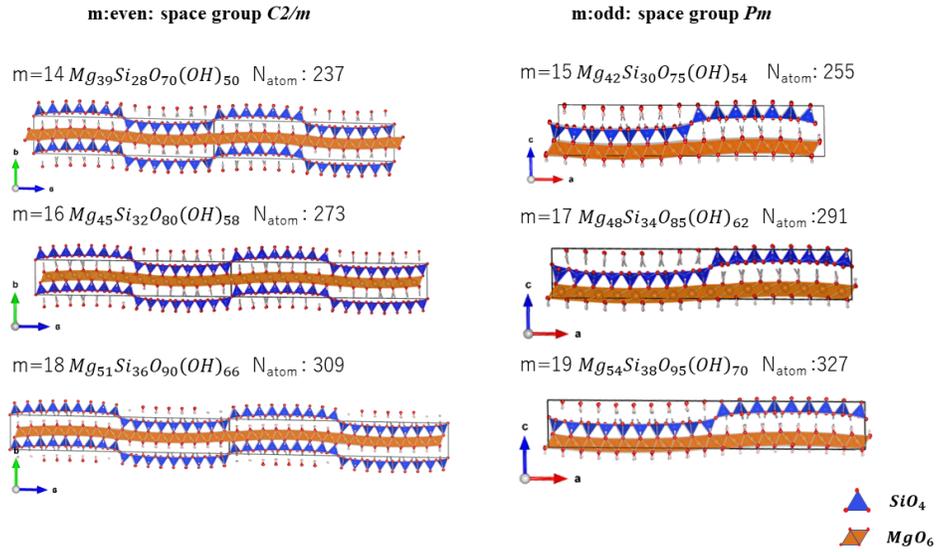
Here $Antigorite_m$ indicates the chemical formula of antigorite with modulation of m which is defined as $Mg_{3m-3}Si_{2m}O_{5m}(OH)_{4m-6}$. In this study, the enthalpy of ice VIII phase was used to investigate the dehydration reaction. This is because temperature effects are not considered in these calculations.

Since antigorite undergoes a phase transition to a dense hydrous magnesium silicate phase, phase A, under high pressure, the following chemical reaction was also calculated:



Table 1. The Monkhorst-Pack meshes and number of k points used in the calculation.

Phase	k point mesh	number of k points
Antigorite (m :even)	$2 \times 2 \times 2$	4
Antigorite (m :odd)	$1 \times 3 \times 3$	5
Lizardite	$6 \times 6 \times 6$	108
Forsterite	$4 \times 2 \times 4$	54
Brucite	$6 \times 6 \times 4$	72
Phase A	$5 \times 5 \times 5$	63
Clinoenstatite	$4 \times 4 \times 4$	32
Stishovite	$4 \times 4 \times 6$	9
Ice VIII	$6 \times 6 \times 6$	108

**Figure 2.** The model structures of antigorites ($m = 14 \sim 19$). The structures where m is even indicate the primitive cell of the space group $C2/m$.

3 Results and Discussion

3.1 Structure optimization

$Antigorite_m$ has m SiO_4 tetrahedra along the a -axis in the unit cell, while there are two SiO_4 tetrahedra along the a -axis in lizardite. Therefore, the a -axis of the antigorites were normalized to the length of two SiO_4 tetrahedra, the same as lizardite, and denoted as a^* (Figure 1). The pressure variation of the lattice constants of antigorites are shown in Figure 3 and Table 2.

Calculated results indicate that the a^* of antigorite is 3-5% shorter than that of lizardite, and this difference is more pronounced for antigorites with smaller m (Figure 3A). This shrinkage is caused by pinning of the m SiO_4 tetrahedra by the $m-1$ MgO_6 octahedra along the a -axis of antigorite. Without taking into account thermal expansion due to temperature effects, antigorites with smaller m -values are subject to more polyhedral distortion. Natural antigorites with $m=13-24$ have been reported, and those with smaller m -values ($m < 13$) have not been found. This can be interpreted as the SiO_4 polyhedral distortion leads to structural instability of antigorites with small m -value.

There is little dependence on the m -value with respect to the change in the b and c -axes of antigorite. As for lizardite, stable and metastable structures have been reported above approximately 8 GPa (Tsuchiya, 2013). No such metastable structures were found in antigorite. At low pressure, the length of the c -axis of antigorite is slightly smaller than that of lizardite, but above 8 GPa, the c -axis of the stable structure of lizardite is smaller. The higher c -axis compressibility of lizardite relative to that of antigorite has also been confirmed by experiments (Nestora et al., 2010; Hilairet et al., 2006). It was expected that as the m -value of antigorite decreases, the number of Si-O bonds connecting the layers per unit volume increases, causing an increase in density. However, contrary to this expectation, we found that the m -value dependence of the density of antigorite is almost negligible (Figure 3E, Table 2).

The high-pressure structure of $m = 17$ antigorite was reported based on the results of a single-crystal X-ray diffraction experiment (Nestora et al., 2010). The present calculations are in good agreement with these experiments within the accuracy of first-principles calculations based on GGA. GGA calculations typically result in volumes that are a few percent higher than experimental volumes due to slightly underestimated binding energies. The experiment of Nestola et al. (2010) reported softening of the antigorite lattice, especially the c -axis, and increase of the β angle above 6 GPa. However, while softening was observed in the lizardite calculations, our antigorite calculations do not reveal softening when we evaluate the compressibility of the c -axis. Additionally, our antigorite calculations do not indicate an increase in the β -axis at pressures up to 14 GPa.

Overall, we find that within the antigorite lattice, the b -axis is less compressible than the a -axis. The a -axis of antigorite is also more compressible than the a -axis of lizardite. These results are consistent with experiments and are tied to the wavy or corrugated structure of antigorite along the a -axis. We also observed that the compressibility of the a -axis is slightly higher for smaller m -value polysomes of antigorite. Both antigorite and lizardite contain hydrogen bonds along the c -axis which are weaker and therefore more easily compressed than other bonds. The c -axis compressibility of lizardite is higher than that of antigorite because the layers of lizardite are bound together only by hydrogen bonds, whereas antigorite also contains partial Si-O bonds between the layers. Somewhat surprisingly, however, the difference becomes more pronounced at higher pressures. Previous first-principles calculation of lizardite reported that the nature of hydrogen bonds in lizardite changes above 10 GPa (Tsuchiya, 2013), which may be responsible for the higher c -axis compressibility of lizardite, whereas the c -axis of antigorite is already compressed at low pressure and there is no commensurate shift in the nature of hydrogen bonds observed in antigorite at the pressures of this study (0-14 GPa).

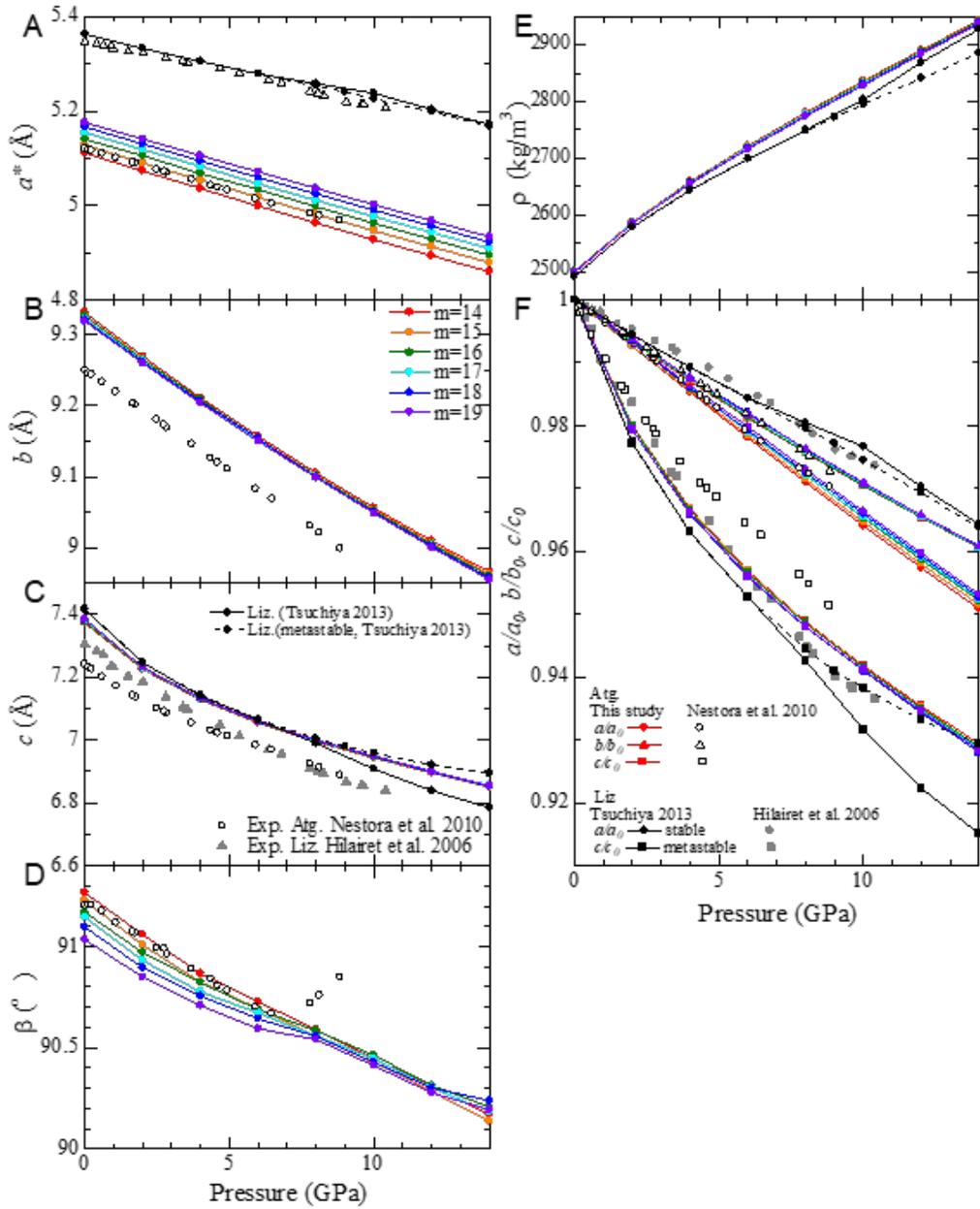


Figure 3. The full colored lines indicate the cell parameters (A~D), density ρ (E) and compressibilities (F) of antigorites ($m = 14-19$). The a^* corresponds to the two SiO_4 polyhedra along the a lengths of Antigorite_m . Black full and dashed lines correspond to the stable and metastable cell lengths of lizardite (Tsuchiya, 2013), respectively. The black-open and full-gray symbols are previous single-crystal X-ray diffraction experiments of antigorite and lizardite, respectively (Nestora et al., 2010; Hilaret et al., 2006).

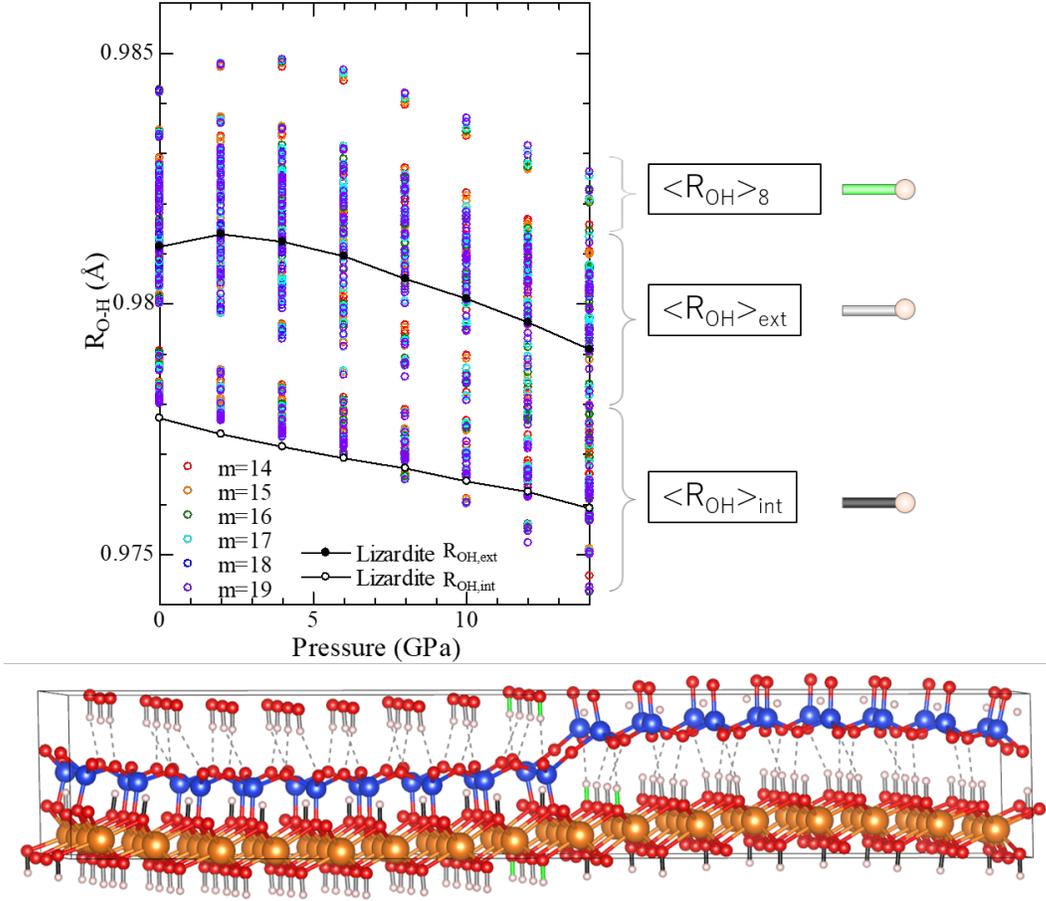


Figure 4. Pressure dependence of the OH distances of antigorites ($m=14-19$). $\langle R_{OH} \rangle_8$ indicates the OH distance oriented to the bridging oxygen atoms between the SiO₄ eight-membered rings (OH bond with green color) at 8-reversals. $\langle R_{OH} \rangle_{int}$ indicates the OH distance in the SiO₄ tetrahedral layers (black bond), and $\langle R_{OH} \rangle_{ext}$ indicates the OH distance oriented toward the interlayer voids (gray bond).

242

243 The pressure-dependence of the OH bond distances within the crystal structure of
 244 antigorite is shown in Figure 4. While lizardite has only two types of the OH bonds, one
 245 within the tetrahedral layers $R_{OH,int}$ and the other between the layers $R_{OH,ext}$, there
 246 are three main groups of OH covalent bonds, reflecting the complexity of antigorite’s crys-
 247 tal structure. Two groups are similar to lizardite; one group of the OH bonds within the
 248 SiO₄ layer ($\langle R_{OH} \rangle_{int}$) and the other between layers ($\langle R_{OH} \rangle_{ext}$). The group unique to
 249 antigorite is the OH bonding group that forms hydrogen bonds to the bridging oxygen
 250 in the SiO₄ 4-membered rings existing at the 8-reversals ($\langle R_{OH} \rangle_8$). The OH bonds in
 251 that group have noticeably longer OH distances than the other two groups, suggesting
 252 that those hydrogen bonds are stronger. Due to the nature of the pseudopotentials used
 253 in this study, our results of the OH distances are longer than those of previous first-principles
 254 calculations conducted for $m=17$ antigorite, but the trend of OH distances at ambient
 255 pressure, $\langle R_{OH} \rangle_8 > \langle R_{OH} \rangle_{ext} > \langle R_{OH} \rangle_{int}$ is consistent (Balan et al., 2021). Although

Table 2. The calculated cell parameters and density (ρ) of antigorite ($m = 14-19$).

Pressure (GPa)	a (Å)	b (Å)	c (Å)	β (°)	ρ (g/cm ³)
$m = 14$					
0	71.5529	9.3320	7.3727	91.267	2.4997
2	71.0224	9.2699	7.2252	91.059	2.5868
4	70.5033	9.2113	7.1277	90.867	2.6581
6	69.9822	9.1569	7.0546	90.728	2.7216
8	69.4775	9.1050	6.9948	90.589	2.7805
10	68.9803	9.0557	6.9435	90.445	2.8366
12	68.5050	9.0092	6.8962	90.309	2.8906
14	68.0333	8.9650	6.8521	90.169	2.9438
$m = 15$					
0	38.4575	9.3281	7.3755	91.228	2.4994
2	38.1727	9.2663	7.2275	91.008	2.5866
4	37.9023	9.2084	7.1293	90.824	2.6574
6	37.6282	9.1537	7.0562	90.693	2.7205
8	37.3586	9.1020	6.9967	90.556	2.7791
10	37.0975	9.0528	6.9446	90.427	2.8349
12	36.8422	9.0061	6.8968	90.284	2.8892
14	36.5926	8.9615	6.8509	90.137	2.9429
$m = 16$					
0	82.2465	9.3273	7.3770	91.171	2.4997
2	81.6855	9.2654	7.2284	90.971	2.5858
4	81.0803	9.2093	7.1298	90.823	2.6570
6	80.5381	9.1528	7.0564	90.688	2.7192
8	79.9587	9.1013	6.9972	90.584	2.7777
10	79.3946	9.0517	6.9456	90.462	2.8336
12	78.8472	9.0046	6.8976	90.313	2.8881
14	78.3113	8.9595	6.8525	90.206	2.9417
$m = 17$					
0	43.8113	9.3231	7.3821	91.146	2.4984
2	43.5058	9.2635	7.2300	90.931	2.5852
4	43.2026	9.2062	7.1310	90.776	2.6558
6	42.8897	9.1523	7.0576	90.673	2.7189
8	42.5893	9.1002	6.9983	90.558	2.7770
10	42.2995	9.0500	6.9476	90.445	2.8320
12	42.0140	9.0022	6.9000	90.304	2.8862
14	41.7239	8.9569	6.8553	90.183	2.9399
$m = 18$					
0	92.9955	9.3215	7.3833	91.096	2.4978
2	92.3451	9.2622	7.2309	90.895	2.5829
4	91.6948	9.2062	7.1317	90.756	2.6534
6	91.0616	9.1540	7.0572	90.643	2.7155
8	90.4388	9.0996	6.9989	90.557	2.7730
10	89.8244	9.0499	6.9477	90.428	2.8302
12	89.2063	9.0019	6.8983	90.301	2.8826
14	88.5949	8.9567	6.8522	90.238	2.9397
$m = 19$					
0	49.1722	9.3196	7.3836	91.034	2.4984
2	48.8375	9.2606	7.2312	90.849	2.5847
4	48.5004	9.2037	7.1332	90.709	2.6546
6	48.1784	9.1502	7.0588	90.594	2.7163
8	47.8444	9.0985	6.9998	90.540	2.7739
10	47.5157	9.0483	6.9488	90.411	2.8292
12	47.1905	9.0001	6.9006	90.277	2.88439
14	46.8673	8.9541	6.8548	90.193	2.9382

there is a slight variation in the values, this trend is similar for all polysome structures of $m=14-19$.

The relationship between the strength of the hydrogen bond and the OH stretching vibration frequency has been investigated in a wide variety of materials, and it is generally believed that the stronger the hydrogen bond, the lower the OH stretching frequency. In the present study, some OH bonds in the 8-reversal are longer than other OH bonds, and the hydrogen bonds in the 8-reversal are considered stronger. First-principles calculations of the lattice vibrations of antigorite ($m=17$) under ambient pressure have been performed (Balan et al., 2021). The OH stretching vibration of antigorite has a broad asymmetric band of $3650-3750\text{ cm}^{-1}$ at ambient pressure, and these OH bonds, which are unique to antigorite, have one of the lowest frequencies among them around 3650 cm^{-1} . This has been suggested to explain the weak and broad shoulder of the OH stretching band observed $\sim 3615\text{ cm}^{-1}$ measured in the IR absorption band (Mellini et al., 2002).

No study has yet published direct, experimental measurements of the OH distances in antigorite under pressure. However, pressure variations in the OH stretching frequencies of lizardite, chrysotile, polygonal serpentine and antigorite have been reported using Raman spectroscopy (Auzende et al., 2004). The OH stretching vibrations attributed to $\langle R_{OH} \rangle_8$ have not yet been reported, but may explain the presence of experimentally determined low vibrational OH bands observed in antigorite at $\sim 3600\text{ cm}^{-1}$, and which have either a negative pressure dependence or which are pressure independent. In previous dehydration experiments on antigorite, it has been reported that dehydration proceeds in two stages in the temperature range of $800-1000\text{ K}$ (Liu et al., 2019; Chollet et al., 2011). It is not difficult to speculate that antigorite dehydration may go through multiple stages with multiple bonding states as the ambient temperature structure contains three groups of OH bonds with different bond strengths.

3.2 Relative enthalpies

Figure 5(A) shows the pressure dependence of relative enthalpies for reactions (1) through (3). Reaction (1) is the change of lizardite to antigorite plus brucite. Since lizardite can be regarded as antigorite with $m = \infty$, the larger the number of m of antigorite, the closer the enthalpy is to that of lizardite, and vice versa. Our results show that the enthalpy of the combination of antigorite ($m = 19$) and brucite is slightly lower than that of lizardite (about $0.2\sim 0.3\text{ kJ/mol}$) between $0-5\text{ GPa}$, but this is within the margin of error of the calculation and the phase stability cannot be evaluated based on such a marginal enthalpy difference. Since lizardite is reported to be the low-temperature phase of antigorite in nature, lizardite should essentially be the stable phase at static 0 K enthalpy. Similar enthalpy results have already been reported by an earlier study (Ghaderi et al., 2015, note that enthalpies in previous literature have been multiplied by m), with antigorite (+ brucite) being stabilized at ambient pressure using GGA, and lizardite appearing as the stable phase using LDA.

In the $\text{Mg}_3\text{Si}_2\text{O}_5(\text{OH})_4$ composition, the stable phase changes from the combination of antigorite plus brucite to the combination of antigorite, forsterite plus H_2O at about 5 GPa . The present calculations were performed at static 0 K , so ice VIII phase was used instead of liquid water, but this would correspond to a reaction that dehydrates above room temperature. Furthermore, at 7.2 GPa , the hydrous phase A (+ enstatite + stishovite + H_2O), known as the high-pressure hydrous phase of antigorite, has a lower enthalpy. This causes the stable region of antigorite to disappear.

The enthalpy values tend to increase with decreasing values of m near ambient pressure. The enthalpy difference between $m = 19$ and 14 of antigorite at ambient pressure was about 1.3 kJ/mol . Antigorites with $m = 13-24$ have been identified in natural samples, and the absence of antigorites with m -values less than 13 may be due to

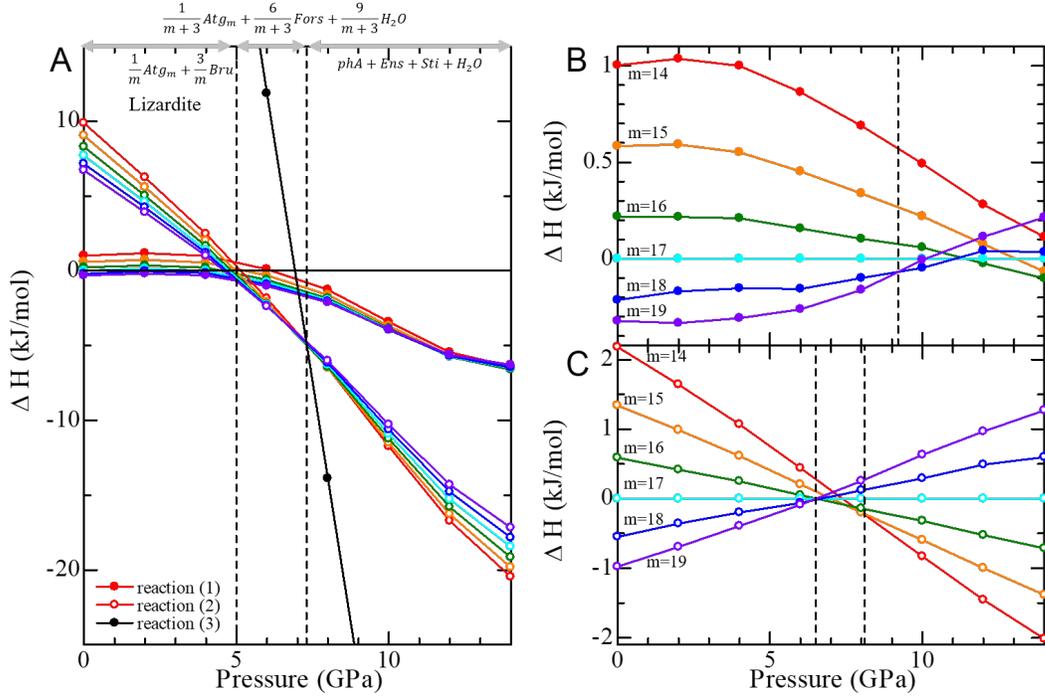


Figure 5. (A) The pressure dependence of the enthalpies of antigorite polysomes with different m -value ($m = 14 \sim 19$) with respect to lizardite ($m = \infty$). The colors in the legend are the same as in Figure 3. Relative enthalpy ΔH is the value of the right-hand side minus the left-hand side of reactions (1)-(3). (B) The ΔH of reaction (1) with respect to right side of reaction (1) for $m=17$, i.e., the enthalpy difference of reaction(1) in (A) rearranged with respect to that of $m=17$ line. (C) The ΔH of reaction (2) with respect to right side of reaction(2) for $m=17$, i.e., the enthalpy difference of reaction (2) in (A) rearranged with respect to that of $m=17$ line.

306 their higher enthalpies. On the other hand, no energetic evidence for the absence of antigorite
 307 with larger m (> 24) was found from the present calculations.

308 The pressure dependence of the enthalpy of antigorite behaves differently depend-
 309 ing on its m -value. In other words, at low pressure conditions, the larger the m (i.e., $m=19$),
 310 the more stable the antigorite. On the other hand, at high pressure, the relationship be-
 311 tween large and small values is reversed (Figure 5 BC). In Reaction (1), the enthalpy value
 312 crossing from $m=19$ to $m=18$ occurs at about 9.2 GPa, and at higher pressures, progres-
 313 sively smaller m antigorites have lower enthalpies. This tendency is more pronounced
 314 in reaction (2), where the enthalpy value change from $m = 19$ to 18 occurs at 6.5 GPa,
 315 and the lowest change to $m = 14$ occurring at 8.1 GPa. Antigorite polysomes with m
 316 = 19 and 14 have water contents of 12.4 wt% and 12.2 wt%, respectively. Although the
 317 difference in water content is slight, the change in m from 19 to 14 requires that the antigorite
 318 releases water.

319

320 4 Geophysical implications

321 In this study, the m -dependence of antigorite under high pressure was investigated
 322 using first-principles calculations, and a comparison of the enthalpies of antigorite polysomes

with different m -values reveal that polysomes with smaller m -values are less stable at low pressure conditions, but become more stable relative to larger m -value polysomes at high pressures. This shift from larger to smaller m -value polysomes being stable occurs in a certain range of pressure. As shown in Figure 5C, the shift in m from 19 to 14 occurs sequentially within a pressure range of about 1.6 GPa, from 6.5 GPa to 8.1 GPa. This change is accompanied by the release of a small amount of water (about 0.05 wt.%) as the m of the antigorite decreases within this pressure range.

Wunder et al., 2001 pointed out that the m -frequency of antigorite may decrease under high temperature conditions. Komabayashi et al., 2005 also reported an m -value of 14 for antigorite synthesized at 2 GPa and 600°C, which is consistent with the results of Wunder et al., 2001. In this study, we did not calculate the free energy of antigorite at high temperatures using first-principles calculations, choosing to focus on relative stability at static 0 K due to limited computer resources. As a result, we found that the stable antigorite polysome structure changes with pressure. Taken together, these results suggest that the most frequent m -value of antigorite may decrease with pressure and temperature during the process of water transport to the Earth's deep interior through oceanic plate subduction. Thus, the dehydration of antigorite would not occur at a single discrete pressure and temperature, but rather the boundary is expected to have a fixed width related to the sequential polysomatism from large to small m -value polysomes.

In this study, calculations are performed only on pure Mg,Si-antigorites and the effects of impurities, especially Al and Fe, are ignored. As mentioned in the introduction, the structure of antigorite is controlled by the misfit between M and T sheets. Therefore, it is highly possible that impurities in these sheets can change the amount of misfit between the sheets and influence the stable polysome of antigorite at a given pressure and temperature. Additionally, as reported based on electron microscopy observations, the enthalpy differences between antigorites with different m -values are so small that antigorites with multiple m -values coexist metastably under finite temperature conditions. The results of our enthalpy calculations indicate that the m -value of the most frequent polysomes varies with pressure, but it is likely that multiple polysomes coexist in each state.

The physical mechanisms of intermediate-depth and deep-focus earthquakes, which occur at P - T conditions that should produce ductile deformation rather than brittle fracture, have been debated because the triggering mechanisms are unexplained. The most commonly cited link to intermediate-depth earthquake activity is dehydration embrittlement. However, laboratory experiments on dehydration embrittlement do not explain all the characteristics of these earthquakes. In particular, the cause of the lower plane of the Wadati-Benioff double seismic zone has yet to be elucidated (Kita & Ferrand, 2018). It may be important to consider the phase boundary and dehydration of antigorite will have a width when discussing the region where deep-focus earthquakes occur. This study points out the possibility that the structure and chemical composition of antigorite in the Earth's interior may differ from that at the Earth's surface. Changes in the chemical composition of antigorite are likely to alter its thermodynamic stability fields. Additional experiments and theoretical calculations are needed to investigate the relationship between the breadth of antigorite stability region and the lower Wadati-Benioff zone.

5 Conclusions

In this study, first-principles calculations were performed for different polysomes ($m=14-19$) of antigorite to determine the crystal structure and enthalpy at 0-14 GPa and 0 K. In the pressure range up to 0-6 GPa, polysomes with larger m ($m=19$) antigorite polysomes were found to be stable, while structures with smaller m ($m=14$) were found to be stable under high pressure above 8 GPa. The m -value of stable antigorite changes gradually in the pressure range in between. Each of these changes is accompanied by slight

374 dehydration. Therefore, the dehydration reaction of antigorite under pressure does not
 375 occur all at once at the phase boundary, but may proceed stepwise with the m change
 376 over a certain pressure range. Such phenomena should be taken into account in study-
 377 ing the relationship between dehydration and dynamic phenomena in serpentine trans-
 378 ported into the Earth’s interior. It is necessary to quantitatively evaluate the dehydra-
 379 tion of these phenomena at high temperatures and to investigate the effects of impuri-
 380 ties such as iron and aluminum in the future.

381 Acknowledgments

382 This work was supported by JSPS KAKENHI Grant Number JP20K04043, JP20K04126
 383 and JP23H01273. The computation was carried out using the General Projects on su-
 384 percomputer "Flow" at Information Technology Center, Nagoya University.

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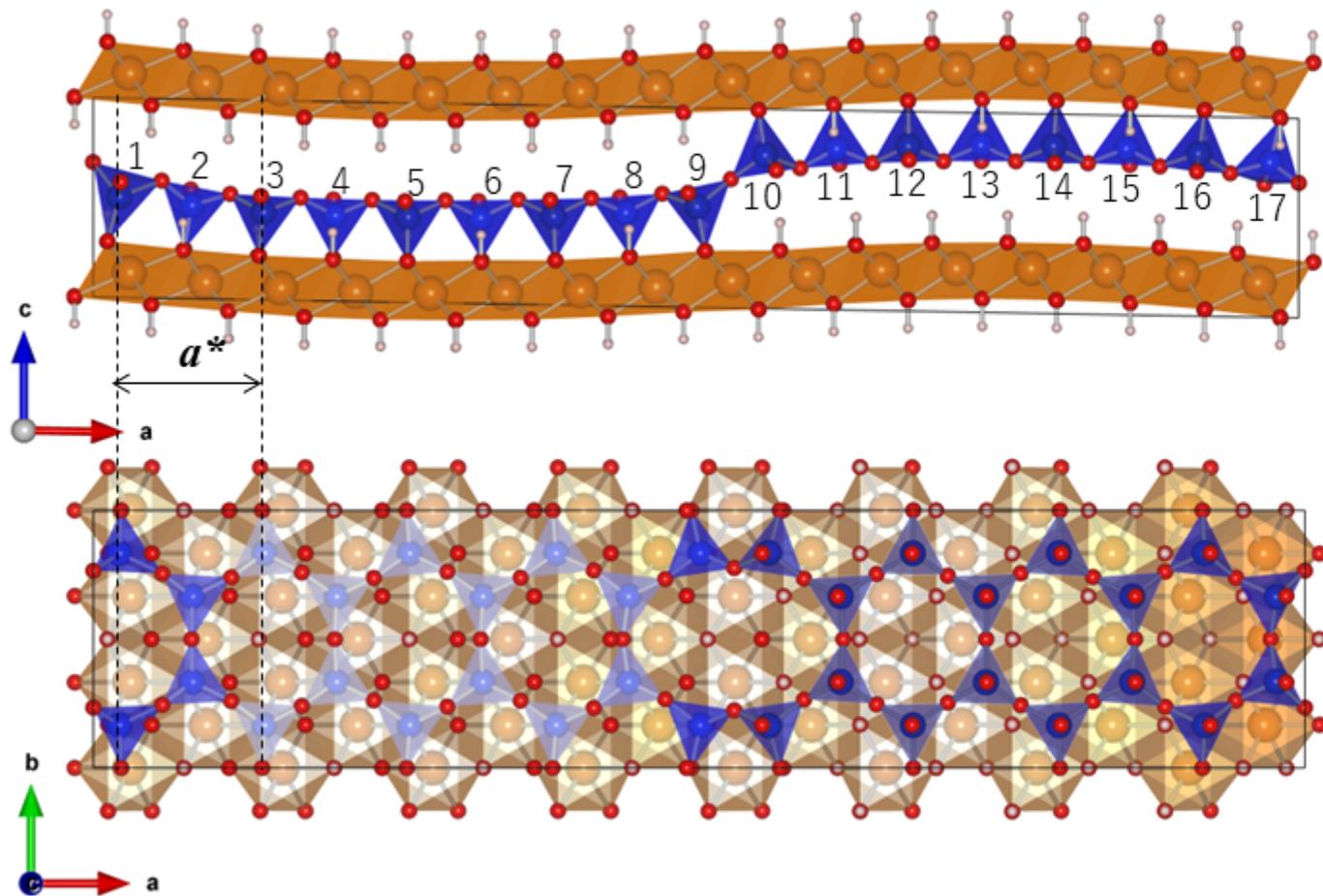
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Figure 1.

Antigorite



Lizardite

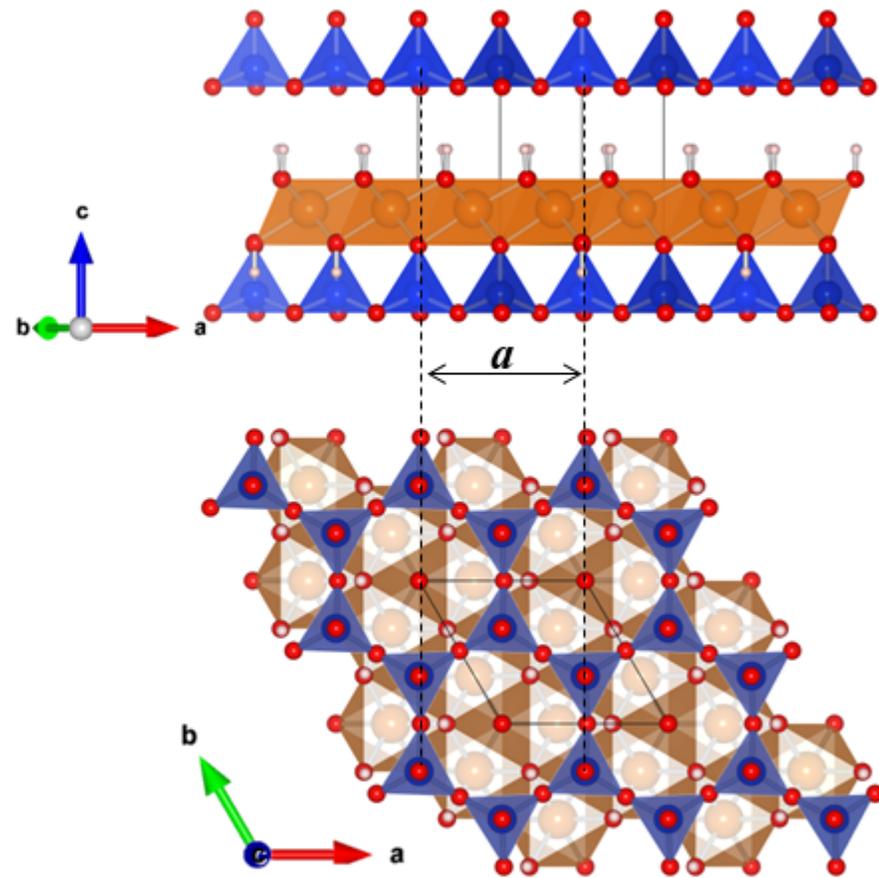
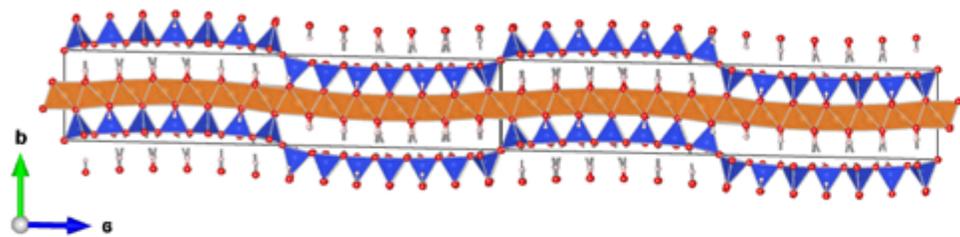


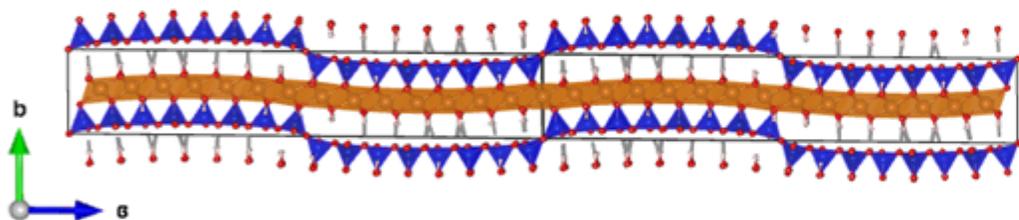
Figure 2.

m:even: space group $C2/m$

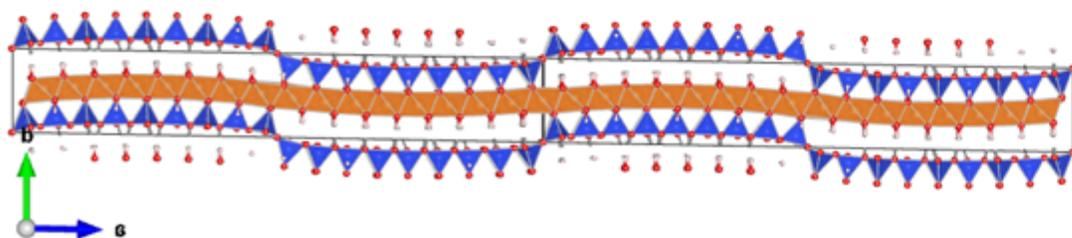
$m=14 Mg_{39}Si_{28}O_{70}(OH)_{50}$ $N_{atom}: 237$



$m=16 Mg_{45}Si_{32}O_{80}(OH)_{58}$ $N_{atom}: 273$

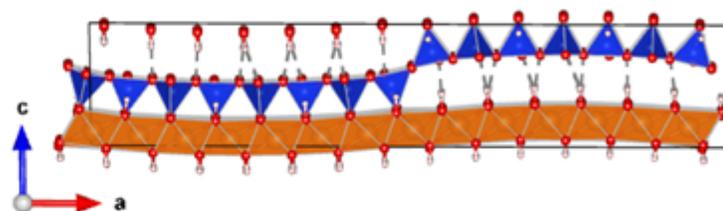


$m=18 Mg_{51}Si_{36}O_{90}(OH)_{66}$ $N_{atom}: 309$

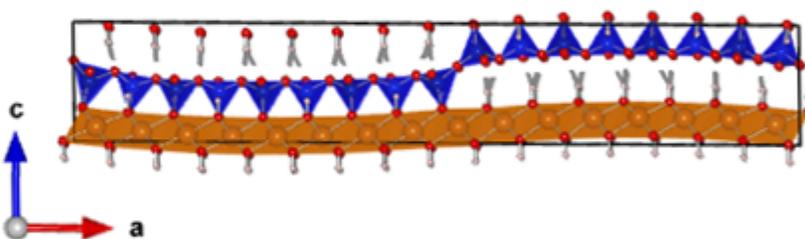


m:odd: space group Pm

$m=15 Mg_{42}Si_{30}O_{75}(OH)_{54}$ $N_{atom}: 255$



$m=17 Mg_{48}Si_{34}O_{85}(OH)_{62}$ $N_{atom}: 291$



$m=19 Mg_{54}Si_{38}O_{95}(OH)_{70}$ $N_{atom}: 327$

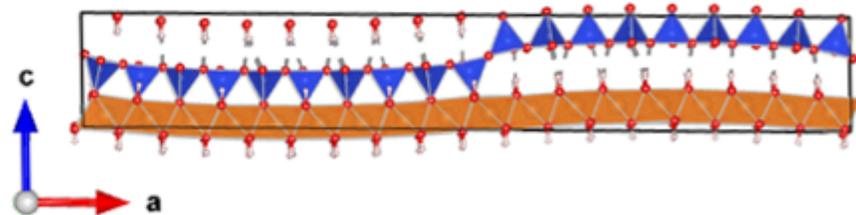


Figure 3.

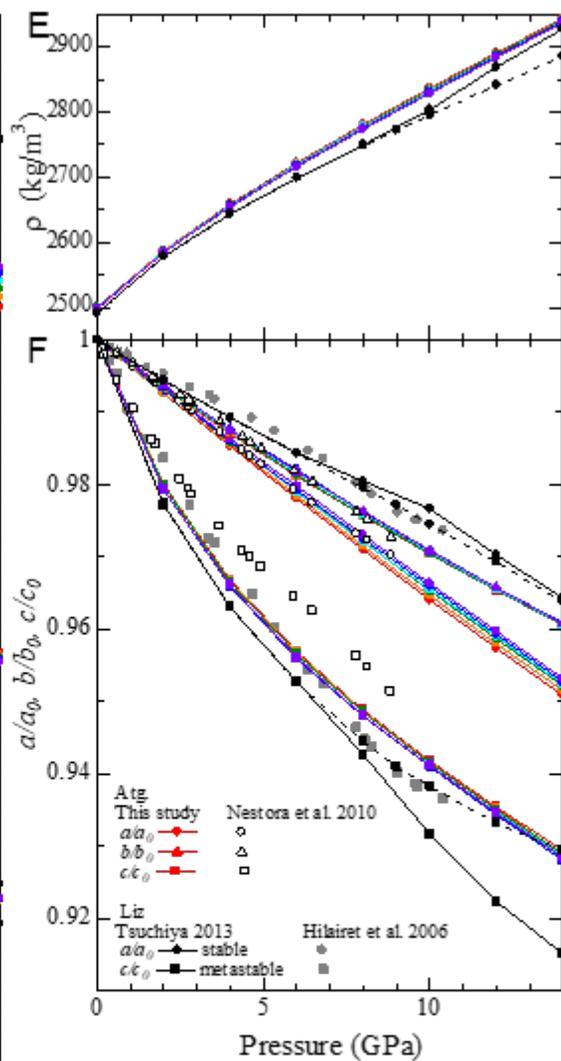
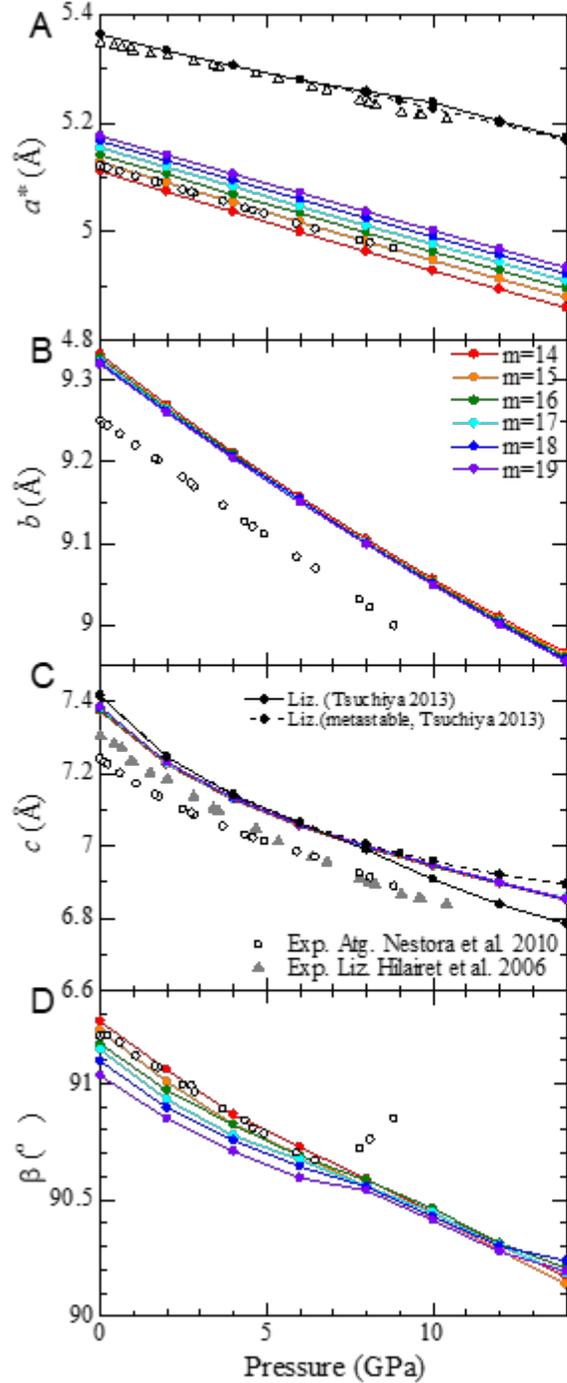


Figure 4.

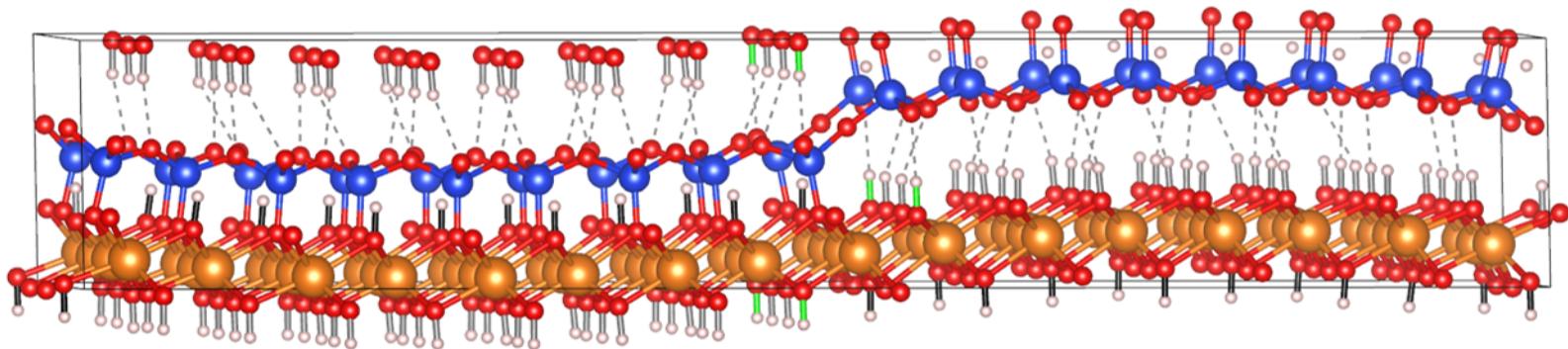
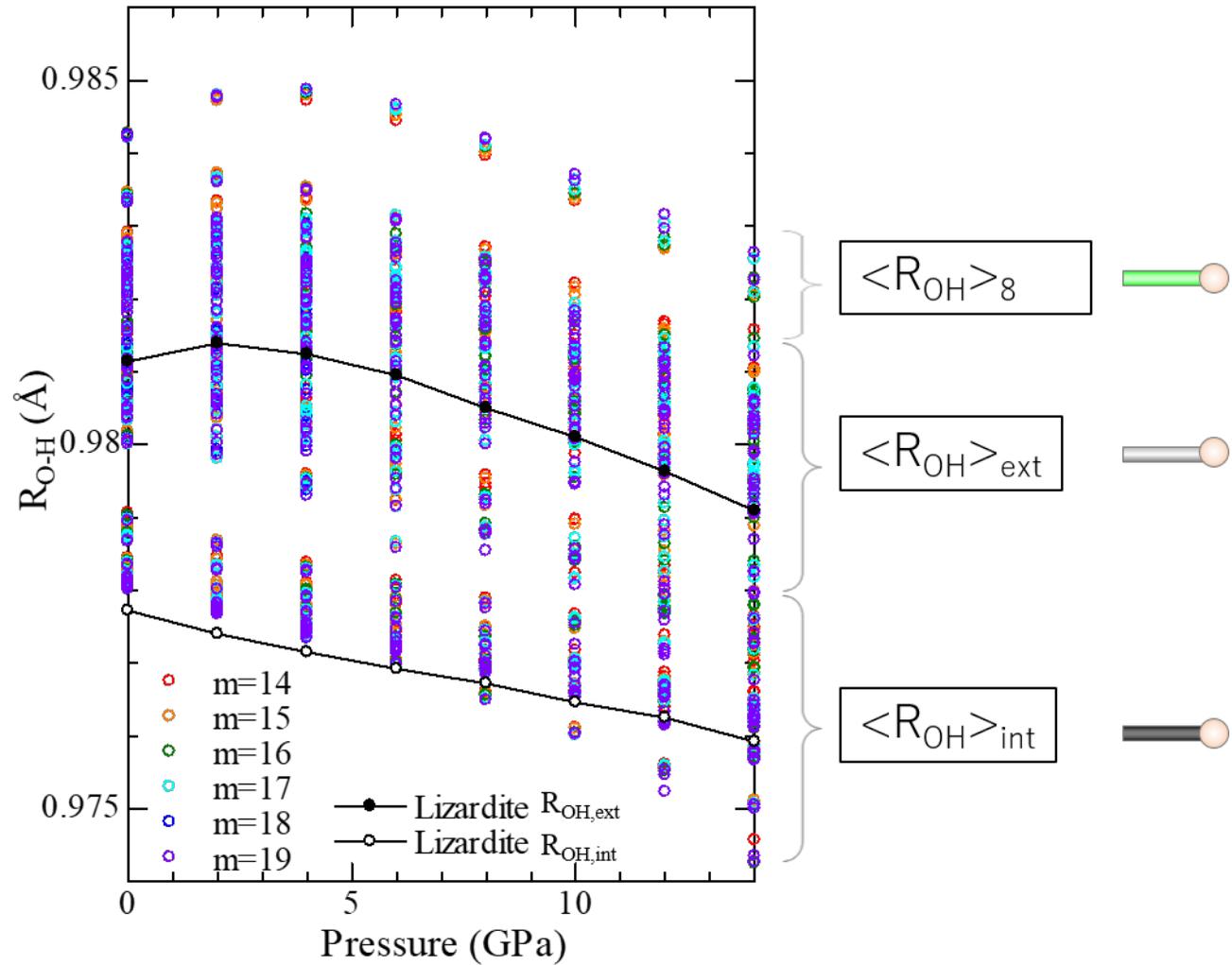


Figure 5.

