

Water in the crystal structure of CaSiO_3 perovskite

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ABSTRACT

While the water storage capacities of the upper 700 km depths of the mantle have been constrained by high-pressure experiments and diamond inclusion studies, the storage capacity of the lower mantle remains controversial. A recent high-pressure experimental study on CaSiO_3 perovskite, which is the third most abundant mineral in the lower mantle, reported possible storage of H_2O up to a few weight percent. However, the substitution mechanism for H in this phase remains unknown. We have conducted a series of density functional theory calculations under static-lattice conditions and high pressures to elucidate hydration mechanisms at the atomic scale. All of the possible dodecahedral ($\text{Ca}^{2+} \rightarrow 2\text{H}^+$) and octahedral ($\text{Si}^{4+} \rightarrow 4\text{H}^+$) substitution configurations for a tetragonal perovskite lattice have very small energy differences, suggesting the coexistence of multiples of H configurations in CaSiO_3 perovskite at mantle pressures and temperatures. The dodecahedral substitutions decrease the bulk modulus, resulting in a smaller unit-cell volume of hydrous CaSiO_3 perovskite under pressure, consistent with the experimental observations. Although the octahedral substitutions also decrease the bulk modulus, they increase the unit-cell volume at 1 bar. The H atoms substituted in the dodecahedral sites develop much less hydrogen bonding with O atoms, leading to a large distortion in the neighboring SiO_6 octahedra. Such distortion may be responsible for the non-cubic peak splittings observed in experiments on hydrous CaSiO_3 perovskite. Our calculated infrared spectra suggest that the observed broad OH modes in CaSiO_3 perovskite can result from the existence of multiples of H configurations in the phase. Combined with the recent experimental results, our study suggests that CaSiO_3 can be an important mineral phase to consider for the H_2O storage in the lower mantle.

Keywords: CaSiO_3 perovskite, water, mantle, first-principles calculation

INTRODUCTION

Global cycles involving volatile elements, such as hydrogen, are important for a range of processes in Earth and planetary systems, including interior-atmosphere interaction, mantle mixing and convection, and surface tectonics (Bolfan-Casanova 2005; Hirschmann 2006; Ohtani et al. 2016). Laboratory studies have shown that some nominally anhydrous minerals (NAMs) in the mantle transition zone can contain a large amount of H_2O in the crystal structure (Kohlstedt et al. 1996; Smyth 1994; Bell and Rossman 1992), which has been recently supported by diamond inclusion studies (Pearson et al. 2014).

However, the H_2O storage capacities of the major nominally anhydrous mineral phases in the lower mantle have been controversial. Earlier studies proposed a possible large storage for bridgmanite (Murakami et al. 2002; Litasov et al. 2003). Later, it was suggested that the existence of small hydrous inclusions can bias the earlier results and that the H_2O storage capacity of bridgmanite is very low compared with the nominally anhydrous mineral phases in the mantle transition zone (Bolfan-Casanova 2005; Panero et al. 2015). However, a more recent study reported a large amount of H_2O stored in bridgmanite crystallized from

melt (Fu et al. 2019). Therefore, the H_2O storage capacity of bridgmanite remains uncertain. It appears that ferropericlase can contain only a very small amount of H_2O (Bolfan-Casanova et al. 2003).

CaSiO_3 perovskite is the third most abundant phase in the pyrolytic lower mantle composition (Kesson et al. 1998; Lee et al. 2004). It is one of the main mineral phases in subducting oceanic crust materials (Hirose et al. 2005; Ricolleau et al. 2010; Grocholski et al. 2012). Inclusions in diamond crystals from the deep mantle support the existence of CaSiO_3 perovskite in the lower mantle (Smith et al. 2018; Nestola et al. 2018). The importance of the crystal structure and elastic properties of CaSiO_3 perovskite has also been highlighted for the topmost lower mantle and the core-mantle boundary region in some recent studies (Thomson et al. 2019; Gréaux et al. 2019). Astrophysical studies have shown that some stars may produce a larger amount of Ca (Hinkel and Unterborn 2018). Earth-like exoplanets around those stars may therefore contain a larger amount of CaSiO_3 perovskite in their lower mantle. Accordingly, it is important to measure possible storage of H_2O and its impact on the equation of state for understanding the geophysics and geochemistry of those planets. Although some studies have suggested possible H_2O storage in this mineral phase (Murakami et al. 2002; Németh et al. 2017; Chen et al. 2020), it has been difficult to characterize the amount

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of H_2O possibly stored in the mineral. The main reason has been that CaSiO_3 perovskite is not quenchable to 1 bar, which makes it difficult to conduct H quantification (such as secondary ion mass spectrometry, SIMS) as the technique requires the recovery of high-pressure samples to 1 bar.

In the most recent experimental study, Chen et al. (2020) proposed a percent level solubility of H_2O in the crystal structure of CaSiO_3 perovskite. Hampered by the amorphization and the limitations in characterization techniques, the quantity and substitution mechanism remain unclear. Nevertheless, they observed several important changes in CaSiO_3 perovskite upon hydration at high pressures. In particular: (1) H substitution is found to decrease the unit-cell volume of CaSiO_3 perovskite, and (2) tetragonal distortion persists to mantle-related temperatures for hydrous CaSiO_3 perovskite. The latter behavior is in contrast with observations for anhydrous CaSiO_3 perovskite in that stability of cubic structure has been known at mantle-related temperatures (Kurashina et al. 2004; Chen et al. 2018). Chen et al. (2020) also found the formation of $\delta\text{-AlOOH}$ in an experiment where Al-bearing CaSiO_3 was heated in an H_2O medium. The result indicates that H_2O changes the partition behavior of Al such that Al does not dissolve in CaSiO_3 in the presence of H_2O , unlike an anhydrous system where up to 10 wt% solubility of Al has been documented (Gréaux et al. 2011). The observation also suggests that $\text{Si}^{4+} \rightarrow \text{Al}^{3+} + \text{H}^+$ mechanism (Pawley et al. 1993; Navrotsky 1999; Litasov et al. 2003, 2007) would not be a major factor for the storage of H_2O in the case of CaSiO_3 perovskite and direct substitution of Ca ($\text{Ca}^{2+} \rightarrow 2\text{H}^+$) (Beran et al. 1996) and Si ($\text{Si}^{4+} \rightarrow 4\text{H}^+$) (Spektor et al. 2011) should be considered. However, because of the experimental difficulties, most notably the inability of X-ray diffraction to directly resolve H atom locations, these experiments could not confirm the H substitution hypothesis in CaSiO_3 perovskite. Density functional theory (DFT) based simulation provides an important tool to examine such proposed substitution mechanisms. The calculation can also address if H_2O substitution can lead to the observed changes in unit-cell parameters and symmetry of CaSiO_3 perovskite in Chen et al. (2020). While DFT methods have been used for studying the physical properties and crystal structure of CaSiO_3 perovskite (Chizmeshya et al. 1996; Akber-Knutson et al. 2002; Magyari-Köpe et al. 2002; Jung and Oganov 2005; Caracas et al. 2005; Stixrude et al. 2007; Kawai and Tsuchiya 2015; Thomson et al. 2019), to our knowledge, there is no DFT study examining the possible substitution of H_2O in CaSiO_3 perovskite. MgSiO_3 perovskite (bridgmanite) has a similar structure with a lower symmetry (orthorhombic). Hernández et al. (2013) has conducted DFT calculation for H substitution in bridgmanite. However, they focused primarily on the partitioning of H among bridgmanite, ringwoodite, and periclase, and only one configuration was used to represent each of the dodecahedral and the octahedral substitutions.

In this study, we explore the energetics and impact of $\text{Ca}^{2+} \rightarrow 2\text{H}^+$ and $\text{Si}^{4+} \rightarrow 4\text{H}^+$ substitutions on the energetics and the crystal structure of CaSiO_3 perovskite. The focus of our study is to examine if the experimentally observed changes in unit-cell parameters and symmetry of CaSiO_3 perovskite can be explained by these substitution mechanisms. In addition, we calculated infrared spectra of a few chosen H configurations

and compared them with the reported IR spectra for the OH vibration in CaSiO_3 perovskite.

METHODS

Density functional theory calculation

We conducted the density functional theory (DFT) calculations using both the GPAW code (Enkovaara et al. 2010) and the VASP code (Kresse and Furthmüller 1996) with generalized gradient approximations (GGA) for the exchange correlation potentials. For GGA we used PBE exchange-correlation functional (Perdew et al. 1996). For the projected augmented wave (PAW) (Blöchl 1994) method adopted here, a plane-wave cutoff of 1000 eV was sufficient to converge the unit cell electronic energy to the meV level and reduce the residual atomic forces to 0.03 eV/Å. We tested the calculations for a higher cutoff energy (1200 eV) and a lower residual atomic forces (0.01 eV/Å). We found negligible changes in these tests, such as less than 0.0006 Å changes in unit-cell parameters, 0.01 Å changes in the bond distances, and 0.02° changes in the bond angles. The outcomes obtained from GPAW and VASP were found to be essentially indistinguishable.

We adapted the tetragonal structure reported in Chen et al. (2018) for the anhydrous CaSiO_3 perovskite model. The space group of the initial model structure is $I4/mcm$ with $\sim 7^\circ$ antiphase rotations of the octahedra in the framework with rotation vectors along one primary axis—the $a0a0c$ —rotation group in the Glazer notation (Glazer 1972). The c -axis is doubled compared to the perovskite aristotype. We constructed a $2 \times 2 \times 1$ supercell of the tetragonal cell and then removed all the symmetry constraints for calculations of a $P1$ cell. Therefore, our “Anhy” model cell contains a total of 80 atoms (or 16CaSiO_3). We used Monkhorst-Pack sampling (Monkhorst and Pack 1976): a total of 96 points ($4 \times 4 \times 6$). A greater sampling for $(6 \times 6 \times 8)$ did not lead to any significant difference in the crystal structure results. We conducted simultaneous optimization for the atomic positions and lattice constants using the Broyden-Fletcher-Goldfarb-Shanno algorithm (BFGS) in the Atomic Simulation Environment (Hjorth Larsen et al. 2017) in the static lattice approximation (e.g., no zero-point motion or thermal corrections). The calculations were conducted at seven different pressures: 0, 20, 40, 60, 80, 100, and 120 GPa.

Hydrogen substitution models

For storage of H_2O in CaSiO_3 perovskite, we consider two possible substitution mechanisms: dodecahedral Ca substitution (hereafter CaH models),



and octahedral Si substitution (hereafter SiH models),



The Ca and Si substitutions result in 0.99 and 1.96 wt% H_2O in the crystal structure of CaSiO_3 supercell considered in this study, respectively. We also examined two Ca vacancies for two CaH models (see below). The content of H_2O in this case is 2.02 wt%.

In the CaH models, two H atoms bond with two O atoms out of 12 O atoms in a dodecahedral site (Fig. 1). From the symmetry of the Ca-O dodecahedron in the tetragonal perovskite structure expected for anhydrous CaSiO_3 , we identified three groups of O atoms (“S,” “E,” and “L”). For each of the “S” and “L” cases, the four O atoms form a tetrahedral motif as depicted by different colors in Figure 1. The “S” and “L” O atoms are distinguished by their distances from the dodecahedral center where a Ca atom exists. Two of those four O atoms (S or L) can form bonding with two H atoms, resulting in two different cases: H atoms bond with: (1) two O atoms at the same z locations (such as S1-S2, S3-S4, L5-L6, and L7-L8 in the figure; CaH-SS or CaH-LL in Table 1), and (2) two O atoms at the different z locations (such as S1-S3, S1-S4, L5-L7, and L5-L8; CaH-SS’ or CaH-LL’).

The O atoms in the third group have intermediate distances from the center of the dodecahedron (E’s in Fig. 1). They form a square. Considering degeneracy, there are two cases to consider: H atoms bond with: (1) two O atoms at the opposite corners (such as E9-E10; CaH-EE2 where 2 means second neighbor) and (2) two O atoms at the same edge (such as E9-E11; CaH-EE where absence of any number at the end means next neighbor).

We also consider cases where two H atoms bond with O atoms in different groups (Table 1). For example, CaH-SE2 has H atoms bonded to O(S) and O(E) at the second neighbor, such as S1-E9. CaH-SL’3 has H atoms bonded to O(S) and O(L) in two layers separated by O(E) atoms, and they are third neighbors, such as S1-L7 in Figure 1. For some cases, which will be discussed later in this paper,

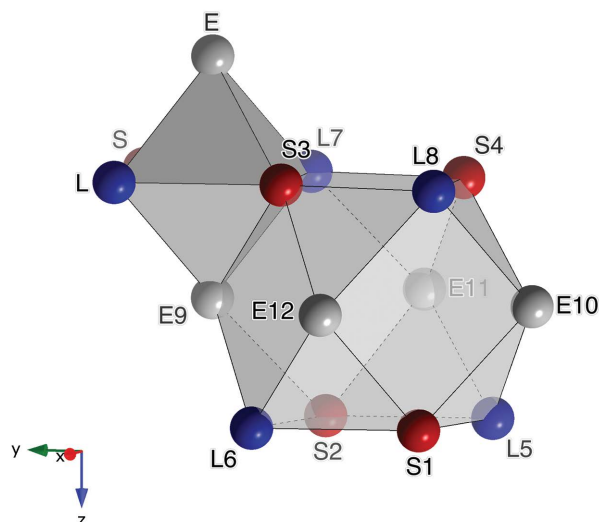


FIGURE 1. The dodecahedral arrangement of O atoms around a Ca atom (not shown for clarity) and the octahedral arrangement of O atoms around a Si atom (not shown for clarity) in CaSiO₃ perovskite for the consideration of H docking sites. The O atoms with the “S,” “E,” and “L” labels are for the atoms at shorter (red), intermediate (gray; at equatorial plane of the dodecahedron), and longer (blue) distances. For a Si vacancy, “S” and “L” are identical to each other because those O atoms are coordinated with neighboring Ca atoms at both short and long distances. (Color online.)

“S” and “L” O atoms become indistinguishable after optimization. We identified 10 energetically distinct structures for the CaH model group as shown in Table 1.

For the octahedral site hydration models (Eq. 2), we have identified four possible configurations for H substitution (Table 1). Because O atoms at both S and L in an octahedron are bonded with neighboring Ca atoms at both distances, these O atoms are no longer distinct with each other and therefore SiH-SSLE is, for example, equivalent to SiH-LLSE. However, SLEE and SSEE are distinct

TABLE 1. Energies calculated for variety of H substitution configurations at 0 GPa and static conditions

Model	Degeneracy	ΔE (meV)
CaH-SS' (or LL') ^a	4	0
CaH-SE2 (or LE2) ^a	8	6
CaH-SL'2	4	32
CaH-SS (or LL) ^a	2	33
CaH-EE ^a	4	86
CaH-SL'3 ^a	4	220
CaH-EE2 ^a	2	236
CaH-SL	8	377
CaH-SE	8	401
CaH-LE	8	405
SiH-SSLE (or LLSE) ^a	8	0
SiH-SLL ^a	1	190
SiH-SSEE (or LLEE) ^a	2	350
SiH-SLEE	4	410

Notes: The CaH and SiH models are for the dodecahedral (a total of 81 atoms in the cell) and the octahedral (a total of 83 atoms in the cell) substitution configurations, respectively. S, E, and L represent O atoms at shorter distances, intermediate distances, and longer distances from the dodecahedral center, respectively. Degeneracy = degeneracy for different H coordinations. Static lattice energies (e.g., neglecting zero-point energy) are listed relative to the lowest energy structure (denoted as $\Delta E = 0$) in the “CaH” and “SiH” models.

' is to note an O atom at a different z (such as S1 and S4 in Fig. 1). Numbers 2 and 3 after the O notations indicate second and third neighbors between the O atoms. If a number is not provided there, it means those O atoms are next neighbors. The models which become identical to each other after optimization are shown in parentheses.

^a Indicates models used for high-pressure calculations.

configurations. The O atoms at L and S are located in the equatorial plane of an octahedron as shown in Figure 2. Two O(S)'s are located diagonal positions in the plane. Therefore, in SLEE, H atoms bond to two neighboring O atoms in the plane, while in SSEE, H atoms bond to O atoms at the diagonal positions (SLEE is the most energetically unfavorable SiH configuration).

The starting crystal structures for the hydration models were constructed from the optimized anhydrous CaSiO₃ perovskite model. We removed Ca or Si atoms to create defects from the anhydrous structure and then added compensating H atoms at 1 Å away from the covalently bonded O atoms. The starting models of CaH assume that H atoms point to the center of the dodecahedral site from the docking O atoms. In the SiH starting models, the H atoms point at adjacent O atoms in the octahedral sites. If H-unbonded O atoms are available in the octahedron, H atoms are aligned to point to those O atoms.

The structures were calculated by relaxing all atomic positions (including H), cell shape, and unit-cell volume. We conducted calculations for the same computational conditions employed in the anhydrous model above (Table 1). While initially distinct, some models become identical to each other after optimization, such as CaH-SS' and CaH-LL', and CaH-SS and CaH-LL, as noted in the table. Also, we found that SiH-SLL structure becomes SiH-SSLE at 20 GPa. For the purpose of understanding the impact of higher concentration of H defects on CaH configurations, we conducted calculations for CaH-EE2 and CaH-SL'3, which are CaH-EE2 $\times$ 2 and CaH-SL'3 $\times$ 2, respectively.

The pressure-volume data we obtained from the DFT calculations were fit to Vinet equation (Vinet et al. 1989) for the effects of H₂O substitution on the compressibility of CaSiO₃ perovskite. To simplify the comparison, we first conducted fitting for bulk modulus (K_0) only while fixing unit-cell volume at 1 bar (V_0) to the calculated values and pressure derivative of K_0 (K'_0) to 4.45, which was obtained for the anhydrous case (Table 2). We also conducted fitting for both K_0 and K'_0 . The fitting was conducted using the Pytheos package (Shim 2017). The K_0 and K'_0 we obtained for anhydrous CaSiO₃ perovskite are in agreement with previous studies (Chizmeshya et al. 1996; Akber-Knutson et al. 2002; Magyari-Köpe et al. 2002; Jung and Oganov 2005; Kawai and Tsuchiya 2015; Noguchi et al. 2013; Chen et al. 2018).

Calculation of infrared spectra

The infrared intensities were obtained by first re-optimizing the desired structural model to a high degree of convergence (residual cell stress and atomic forces <0.01 kbar and 0.0001 eV/Å, respectively), and then calculating the Γ -point phonon frequencies and corresponding displacement vectors using density functional perturbation theory as implemented in the VASP code. In this part of the procedure, the dielectric response and Born effective charge tensor were systematically obtained (using the LEPSILON flag), then combined with the Γ -point phonon eigenvectors to obtain the infrared intensity of each mode (Porezag and Pederson 1996). The resulting discrete spectra were then convoluted with a Gaussian function (width of 50 cm⁻¹).

RESULTS AND DISCUSSION

Energetics of the hydrogen substitutions in CaSiO₃ perovskite

As shown in Table 1 and Figure 3, the enthalpy difference between CaH models is smaller than ~ 1.5 meV per atom for the pressure range we considered. This energy difference corresponds to 36 K and, therefore all the configurations we consider here are plausible for the H substitution mechanism and multiples of different H configurations considered here may coexist at mantle pressures and temperatures.

Among the models we studied, the CaH-EE2 model is similar to the arrangement of H atoms proposed for natural hydrous CaTiO₃ perovskite by Beran et al. (1996). The enthalpy for the structure was the highest among the model we studied. Although details were not provided, a stable H configuration in the dodecahedral site reported for bridgmanite in Hernández et al. (2013) appears to be similar to CaH-SS', which is the most stable H configuration in our study (Fig. 3a).

SiH-SSEE has somewhat higher enthalpy than SiH-SSLE, at

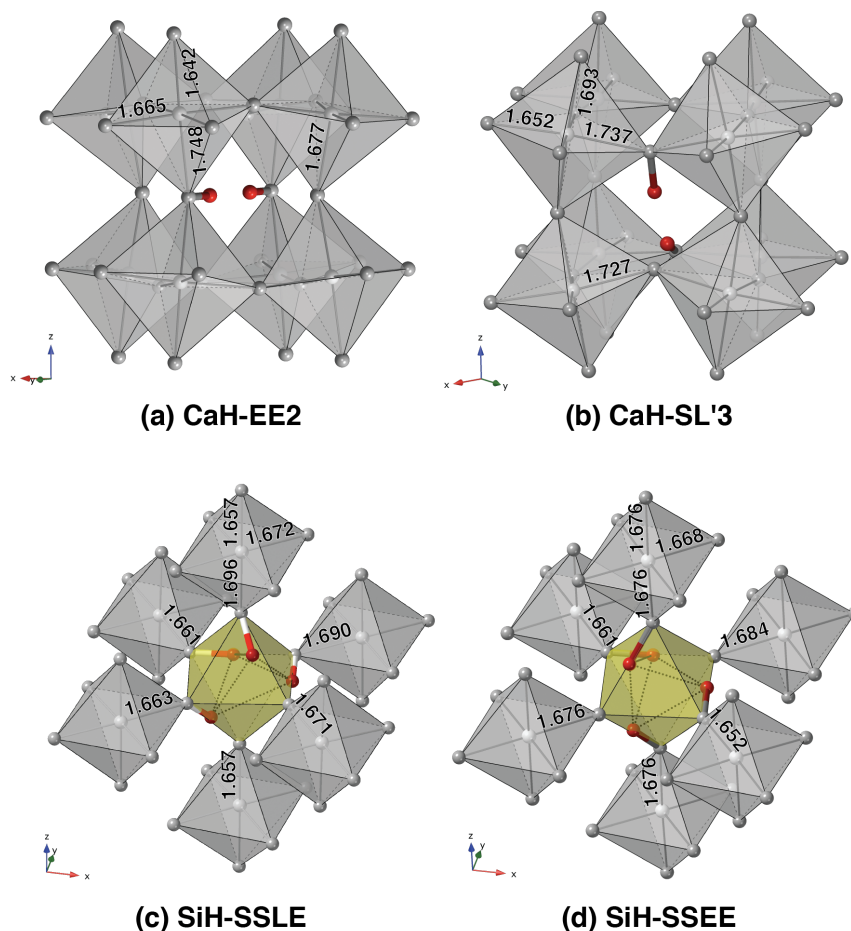


FIGURE 2. Crystal structure of hydrous CaSiO_3 perovskite obtained from calculation results at 100 GPa: (a and b) the dodecahedral site hydration models (Eq. 1) and (c and d) the octahedral site hydration models (Eq. 2). More information on the hydrogen substitution models can be found in Table 1. Light and dark gray spheres are Si and O atoms, respectively. Red spheres are H atoms. In c and d, the yellow octahedron at the center is the Si defect site for hydration. In these diagrams, the dashed lines connect four H atoms, which forms a tetrahedral shape. The numbers are the Si-O bond distances in angstroms. (Color online.)

lower pressures while the enthalpy difference between the SiH-SSLE and SiH-SSEE models changes with compression (Fig. 3b). H configurations similar to SiH-SSEE was documented as the lowest energy one alongside with SiH-SSLL (which transforms to SiH-SSLE at 20 GPa for CaSiO_3 perovskite) for bridgmanite in Hernández et al. (2013). SiH-SSEE is similar to the H configuration proposed for H in hydrous stishovite by Spektor et al. (2011). In this configuration, four out of six O atoms in an SiO_6 octahedron are bonded to H atoms and the other two remain unbonded to H. The four H atoms point at H-unbonded O atoms and they form a tetrahedron (the dotted lines in Fig. 2d). In SiH-SSEE, the centroids of the 4H polyhedron and the 6 O octahedron match well. However, they are about 0.2 Å off from each other in Si-SSLE. The most notable difference between these two structures is that the average H-H distance is greater in SiH-SSLE at lower pressures compared with SiH-SSEE (Fig. 4). This can be seen in the histograms in Figure 5, which also show a much broader range of H-H distances in SSLE than SSEE. Among the broad range, SSLE shows very long H-H distances at lower pressures, which may explain the slightly lower energy of

the structure at lower pressures. The observation suggests that the smaller H-H distance and therefore stronger repulsion between them could make the SSEE configuration less stable than SSLE at lower pressures in CaSiO_3 perovskite.

However, SiH-SSLE becomes slightly more stable with compression because of the effects from the H-H distances.

Unit-cell parameters and compressibility

Chen et al. (2020) found that hydrous CaSiO_3 perovskite has a smaller unit-cell volume than anhydrous CaSiO_3 perovskite. They also showed that the splitting of the 200 peak (the Miller index is for a pseudo-cubic cell) persists to mantle-related temperatures, suggesting the stabilization of a tetragonal structure at the conditions in the hydrous case. This observation is in sharp contrast with anhydrous CaSiO_3 perovskite where stability of a cubic structure has been found at mantle-related temperatures and high pressures (Kurashina et al. 2004; Chen et al. 2018).

Our results show that the unit-cell volume of hydrous CaSiO_3 perovskite does not change more than 0.07% from that of anhydrous CaSiO_3 perovskite at 1 bar for CaH (Fig. 6a). In the case

TABLE 2. Equation of state parameters for anhydrous and hydrous CaSiO_3 perovskite obtained from fitting to Vinet equation

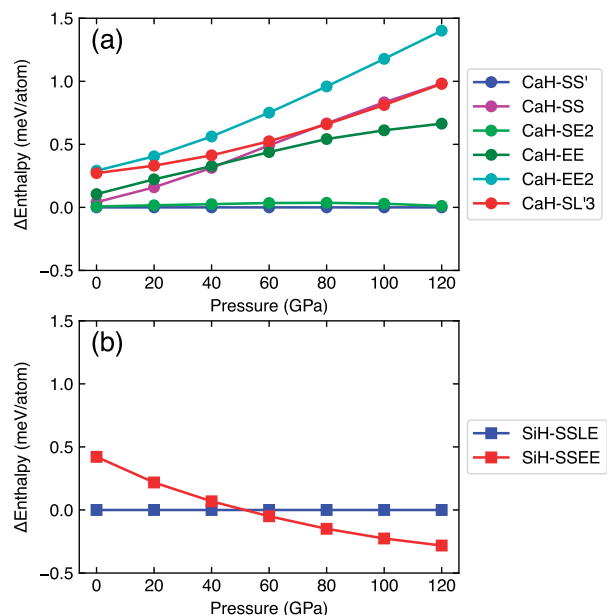
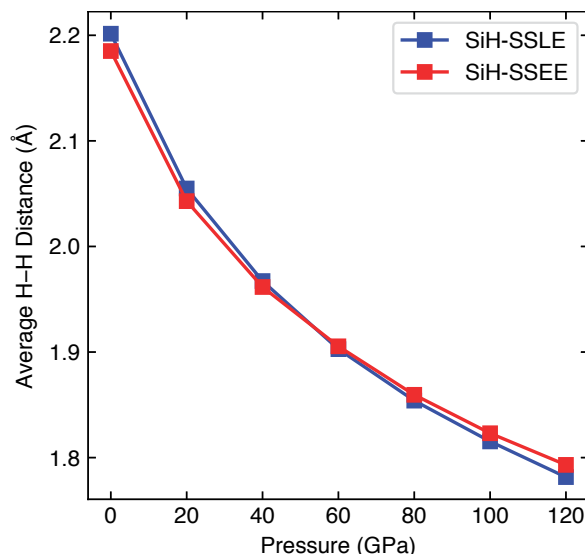
Model	V_0 ($\text{\AA}^3$)	K_0^* (GPa)	K_0 (GPa)	K_0'
Anhy	47.392	211.72(4)	211.7(3)	4.45(1)
CaH-SS'	47.393	203.36(5)	202.9(3)	4.47(1)
CaH-SS	47.428	204.61(7)	205.5(1)	4.41(1)
CaH-SE2	47.389	203.26(6)	204.1(2)	4.42(1)
CaH-EE	47.424	203.52(11)	205.0(1)	4.39(1)
CaH-EE2	47.424	205.47(4)	205.0(1)	4.47(1)
CaH-SL'3	47.397	205.27(8)	204.2(4)	4.50(1)
SiH-SSLE	48.217	192.53(34)	187.8(2)	4.64(1)
SiH-SSEE	48.123	193.76(38)	188.5(2)	4.66(1)

Notes: We present two fitting results: (1) pressure-derivative of bulk modulus (K_0') fixed for $K_0' = 4.45$ (K_0^*) and (2) K_0' varied. In the fitting, bulk modulus (K_0) was varied while unit-cell volume at 1 bar (V_0) was fixed. The $K_0' = 4.45$ results make the comparison among the models more straightforward, although this fitting strategy yielded higher estimated uncertainties (numbers in the parentheses).

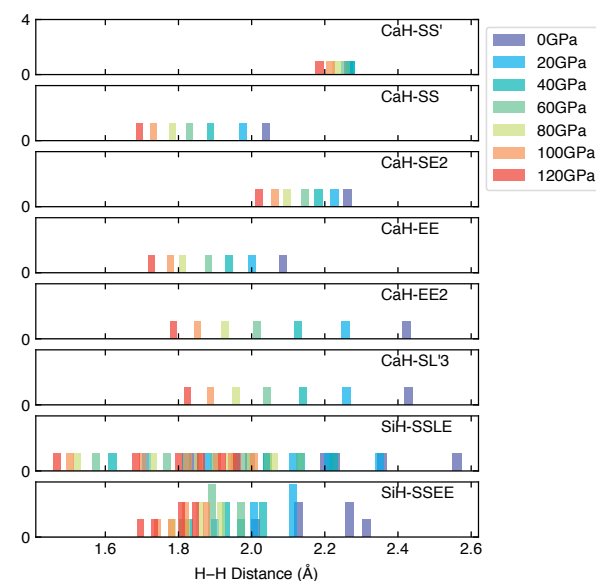
of SiH, we found much larger volume expansion by hydration, more than 1.5%. Previous studies have found that the octahedral site substitution can significantly increase the unit-cell volume of hydrous stishovite (Spektor et al. 2011, 2016; Nisr et al. 2017, 2020). However, the SiH models have twice as much H as the CaH models. We also calculated CaH with two Ca defects for the H substitution, CaH-EE2 $\times 2$ and CaHx2-SL'3 $\times 2$. They both show increases in volume up to 5% at 1 bar, suggesting that more hydration might possibly increase the volume for CaH at 0 GPa.

The unit-cell volume of hydrous CaSiO_3 perovskite becomes smaller than anhydrous case at pressures above 20 GPa for the CaH models (Fig. 6a). The CaH-EE2 $\times 2$ and CaH-SL'3 $\times 2$ models suggest that more hydration would decrease the volume at high pressure even further. Because the SiH models decrease the bulk modulus, the unit cell volumes of hydrous CaSiO_3 perovskite from the SiH models become similar to the anhydrous CaSiO_3 perovskite with an increase in pressure. Both Figure 6a and equation of state fit presented in Table 2 show that H substitution makes CaSiO_3 perovskite more compressible.

From the smaller unit-cell volume of hydrous CaSiO_3

**FIGURE 3.** Enthalpy of (a) CaH models with respect to CaH-SS'. (b) SiH models with respect to SiH-SSLE at high pressures. (Color online.)**FIGURE 4.** The average H-H distances in the SiH models at high pressures. (Color online.)

perovskite observed at high pressure and 300 K, Chen et al. (2020) inferred that the dodecahedral site substitution is more likely than the octahedral site (SiH) substitution because the dodecahedral site (CaH) substitution involves removal of the much larger sized Ca^{2+} . Our DFT calculations found that the dodecahedral site substitution (the CaH models) can result in a smaller unit-cell volume of hydrous CaSiO_3 perovskite at mantle-related pressures, in qualitative agreement with the experimental observation. The experiments found approximately up to 1% reduction in the unit-cell volume at pressures between 2 and 45 GPa. At a similar pressure range, we found 0 to 0.5% decrease in unit-cell volume for 1–2 wt% H_2O in the CaH models. Chen et al. (2020) estimated 0.5–1 wt% H_2O for their samples. Therefore,

**FIGURE 5.** The H-H distances in the models studied. The colors of the bars change from blue to red with an increase in pressure. (Color online.)

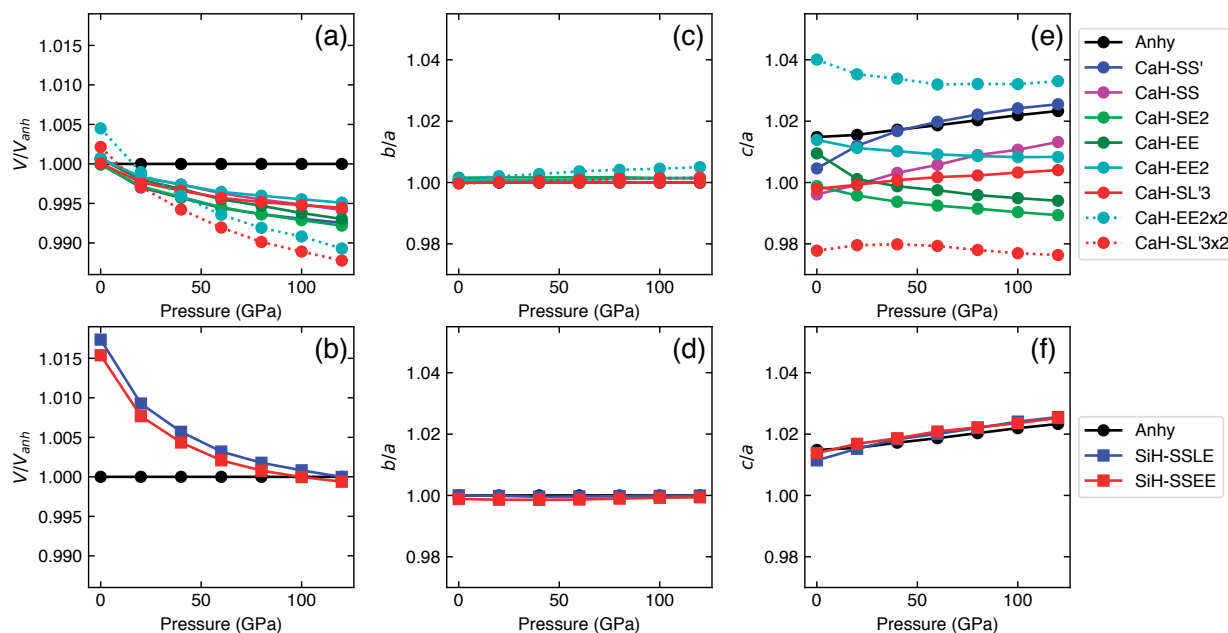


FIGURE 6. Fractional differences in unit-cell volume between hydrous and anhydrous CaSiO_3 perovskite, (a) CaH and (b) SiH models. The b/a ratio for (c) CaH and (d) SiH models. The c/a ratio for (e) CaH and (f) SiH models. (Color online.)

both studies are in general agreement in the magnitude of the changes in unit-cell volume for hydration level of a few percent.

Figure 6b compares the c/a axial ratio of hydrous CaSiO_3 perovskite with anhydrous case. We found a little difference between the a and b axes, suggesting that tetragonal description for the unit cell dimension is acceptable. At 300 K, Chen et al. (2018) reported 1.005 for the c/a ratio in anhydrous CaSiO_3 perovskite. Our DFT calculation suggests 1.02 for anhydrous case at 0 K without zero-point motion. Considering the fact that anhydrous CaSiO_3 perovskite transforms to a cubic structure at high temperature and the ratio, therefore, decreases with temperature, our DFT calculation is in reasonable agreement with the experimental result. Our c/a values agree well with those reported by Stixrude et al. (2007) through DFT calculation between 0 and 140 GPa at 0 K, 1.013–1.020.

Chen et al. (2020) reported persistence of the 200 peak splitting, therefore $c/a \neq 1$, in hydrous CaSiO_3 perovskite at mantle-related temperatures. The observation is in contrast with the known thermal behavior of anhydrous CaSiO_3 perovskite in that the peak splitting disappears, therefore c/a becomes 1, at temperatures greater than ~ 500 K (Kurashina et al. 2004; Chen et al. 2018).

All the hydration models we studied show a significant deviation of c/a from 1. The SiH models show little difference from anhydrous case (Fig. 6b). The CaH-SS', CaH-EE2, and CaH-SS models in general increase the c/a ratio similar to the anhydrous case but the magnitude of the deviation from $c/a = 1$ is smaller. The CaH-SL/3, CaH-EE, and CaH-SE2 models show an opposite effect on the c/a ratio to the anhydrous case. From the comparison between CaH-EE2 and CaH-EE2 $\times 2$ models and between CaH-SL/3 and CaH-SL/3 $\times 2$ models, it can be inferred that more H can increase the deviation of the c/a ratio from 1.

Thermal effects on the c/a ratio were not included in our calculations. So results do not directly address the question of whether the c/a ratio remains different from 1 or the peak splitting is still observable in diffraction patterns at mantle-related temperatures. However, the larger magnitude of distortion found particularly in 2 wt% H_2O CaH cases may suggest that the peak splitting could remain observable at high temperature if the rate of decrease in the c/a ratio toward 1 remains the same in those hydrous cases. However, fundamental reasons that hydrous CaSiO_3 perovskite can be non-cubic at high temperatures will be discussed in the next section.

Bonding between hydrogen and O atoms in hydrous CaSiO_3 perovskite

The tetragonal distortion in the hydrous CaSiO_3 perovskite can be interpreted in two different ways: either by an ordered model that involves the ordering of the hydrogen-bearing defects or a disordered model that results from a structural average of the defects occupied randomly. In this section, we discuss mostly the former case.

For the interpretation based on defect ordering, recent studies have suggested an important role of hydrogen bonding formation ($\text{O} \cdots \text{H}-\text{O}$) and its potential symmetrization ($\text{O}-\text{H}-\text{O}$) for the crystal structure and physical properties of hydrous phases at high pressures and high temperatures, such as hydrous stishovite (Spektor et al. 2011; Nisr et al. 2017), δ - AlOOH (Tsuchiya et al. 2002), and ϵ - FeOOH (Gleason et al. 2013). It is believed that hydrogen bonding forms for a H-to-O distance less than ~ 2 Å (Legon and Millen 1987).

Figure 7a shows histograms of the distances between neighboring O and H atoms in the studied hydration models for CaSiO_3 perovskite. For CaH-SS', CaH-SE2, CaH-SL/3, SiH-SSLE, and

SiH-SSEE, we found increased population of the bond distances between 1 and 2 Å with compression. For example, in CaH-SS' at 120 GPa, an O atom in the dodecahedral site approaches the second-neighbor H within 1.35 Å, while the O-H covalent bond stretches to 1.1 Å. This behavior can be explained by enhanced hydrogen bonding ($\text{O}\cdots\text{H}$) in these structures, leading to the increased population between 1 and 2 Å. As a consequence, the O-H covalent bonding weakens, leading to an increase in the O-H distances. This behavior is more pronounced in the SiH models than the CaH models (reflected in more populations of the bonds between 1 and 2 Å), likely because of the shorter distances among O atoms around the octahedral sites compared with those around the dodecahedral sites.

Figure 7b shows histograms of the $\angle\text{O-H}\cdots\text{O}$ angles within a distance (between O and H) of 2.0 Å. For the CaH-SS' and CaH-SL'3 configurations, the $\text{O-H}\cdots\text{O}$ bond angles remain between 140 and 150° to the highest pressure, while CaH-SE2 develops the $\text{O-H}\cdots\text{O}$ bond angles between 80 and 100°, particularly at pressures higher than 80 GPa. The CaH-SS' and CaH-SE2 configurations are the two lowest enthalpy ones in the CaH group (Fig. 3). Therefore, structures, which can facilitate the formation of stronger hydrogen bonding can be energetically more advantageous. It is notable that CaH-SL'3 has shorter H-H distances (so more H-H repulsion) than CaH-SE2 at 120 GPa (Fig. 5) and less stable configuration (Fig. 3). Therefore, formation of nearly straight $\text{O-H}\cdots\text{O}$ bond may not be as much influential for the stabilization of H in CaSiO_3 perovskite.

In the SiH structures, larger population of shorter $\text{O}\cdots\text{H}$ bonds (or enhanced hydrogen bonding) form with O atoms at 80–120° (Fig. 7). Again, closer distances among O atoms around the octahedral sites are likely the reason. In the case of

$\delta\text{-AlOOH}$ and $\epsilon\text{-FeOOH}$, more straight O-H O bonds have been suggested (Tsuchiya et al. 2002). The bond has been predicted to become symmetric with compression. In these structures, no octahedra are defective of cations, and the H atoms bond with O atoms to form tunnel-like CaCl_2 -type structures. Our calculation shows that more deformed shapes of the defect polyhedron (the octahedron for SiH models and the dodecahedron for the CaH models) can facilitate O atoms to develop closer second neighbor distances with H, and many of those O atoms exist at angles much smaller than 180°.

The bonding between O and H atoms can induce some distortion in the crystal structure of CaSiO_3 perovskite. Figure 8 shows the Si-O bond distances from the models in this study. The anhydrous (Anhy) structure has two groups of Si-O bond distances related to the tetragonal distortion of CaSiO_3 perovskite. Although the Si-O bond distances decrease with pressure, they maintain such grouping in the anhydrous case. Much more broad distribution of the Si-O distances was found in hydrous CaSiO_3 perovskite, while they maintain the same trend of overall population shifting to lower Si-O distances with pressure.

All CaH configurations show a small population of long Si-O bond distances persisting throughout the pressure range we studied as indicated by arrows for CaH-SL'3 as an example in Figure 8. However, such a population does not exist in SiH. In SiH configurations, all O atoms have more similar interactions with H atoms in the defective site because of hydrogen bonding as discussed above and hence introduce less distortion to the Si-O bonding in the neighboring octahedra.

In the CaH models, these long Si-O distances are from the O atoms that are also bonded to H atoms (Si-O-H; see Figs. 2a and 2b). This type of O atoms also exists in the SiH models, but the

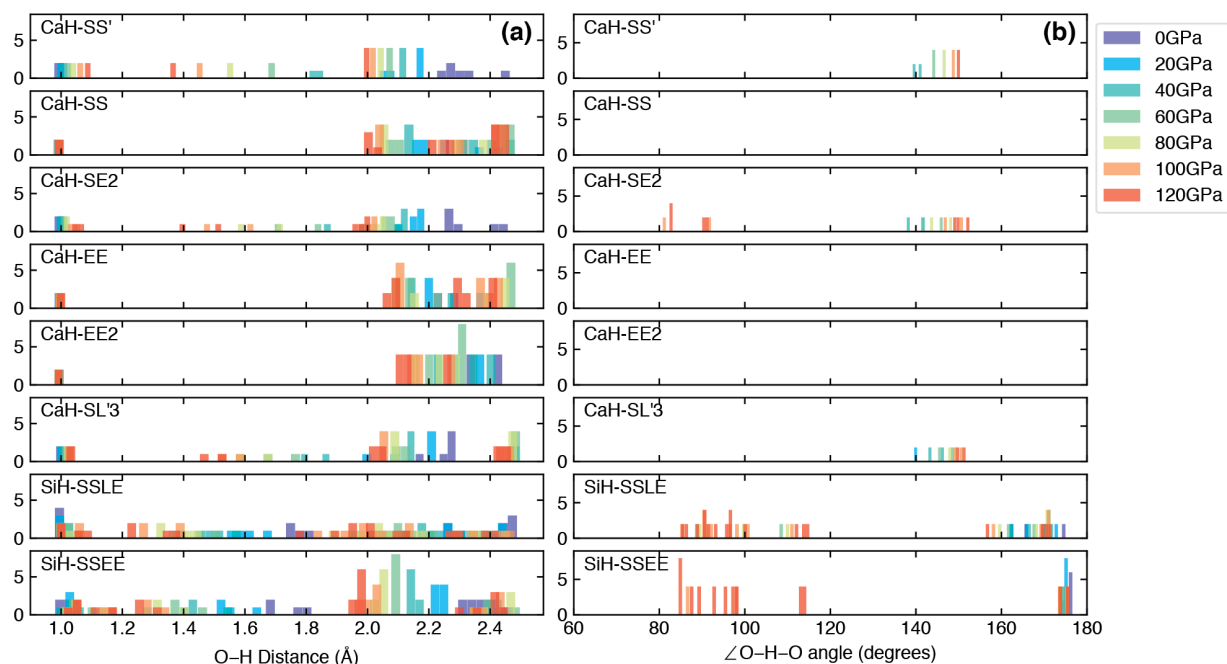


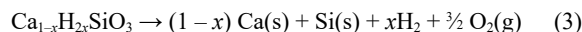
FIGURE 7. (a) Distances between O and H atoms and (b) angles $\text{O-H}\cdots\text{O}$ in the hydration models studied at a range of pressures up to 120 GPa. The colors of the bars change from blue to red with an increase in pressure. Note that no $\text{O}\cdots\text{H}$ bond exists when O-H distances are shorter than 2 Å in CaH-SS, CaH-EE, and CaH-EE2 structures throughout the pressure range investigated. (Color online.)

main difference is that hydrogen bonding occurs to much less of a degree in CaH than in SiH. Therefore, the H atom in CaH weakens the covalent Si-O bonding much more than SiH, and the effect is more preferential for particular O atoms. Consequently, in CaH, the SiO_6 octahedra are much more distorted from their ideal shapes than those in SiH. Such distorted SiO_6 octahedra in the CaH configurations would make hydrous CaSiO_3 perovskite intrinsically non-cubic. This situation would not change with heating as long as OH remains within the structure. This is in contrast to anhydrous case where the tetragonal distortion is mainly from the slight misfit of Ca in the dodecahedral sites at lower temperatures, which ultimately disappears by thermal vibration with heating. Therefore, the experimentally observed persistence of non-cubic peak splitting in diffraction patterns of hydrous CaSiO_3 perovskite can be explained by the intrinsic structural distortion by H substitution (in particular CaH configurations).

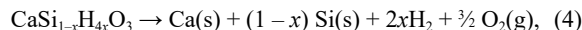
Alternatively, if the symmetry-equivalent H-bearing defects of equal energy are fully disordered, the tetragonal distortion of the perovskite can be due to a change in the apparent average cation sizes in the perovskite. We have noted that the apparent size of Si increases with the substitution of 4H onto Si vacancies, while the apparent size of Ca decreases with the substitution of 2H. Interestingly, if the hydrogen configurations on each defect are randomly distributed in the symmetry-equivalent configurations, the apparent octahedral size changes are isotropic on the scale of the macroscopic crystal sample. This means that the octahedral groups can remain nearly ideal (on average), and the result is that both types of substitution (CaH and SiH) will decrease the tolerance factor of the perovskite, defined as the bond length ratio $(\text{Ca-O})/[\sqrt{2} \times (\text{Si-O})]$. This has the well-known effect of driving the cubic perovskite (tolerance factor ~ 1) toward a tetragonal rotational subgroup (tolerance factor ~ 0.95), similar to the example that is indicated by our data. Our current data cannot distinguish between the disordered possibility described here or the ordered possibilities described above—high-quality crystallographic data on single crystals in the diamond-anvil cell will be required to distinguish between these possibilities.

Energy difference between dodecahedral and octahedral hydrogen substitutions

The relative stability of CaSiO_3 perovskite with the CaH and SiH configurations is determined by their Gibbs energy of formation relative to standard reference states $\text{O}_2(\text{g})$, $\text{Si}(\text{s})$, $\text{H}_2(\text{g})$, and $\text{Ca}(\text{s})$:



and

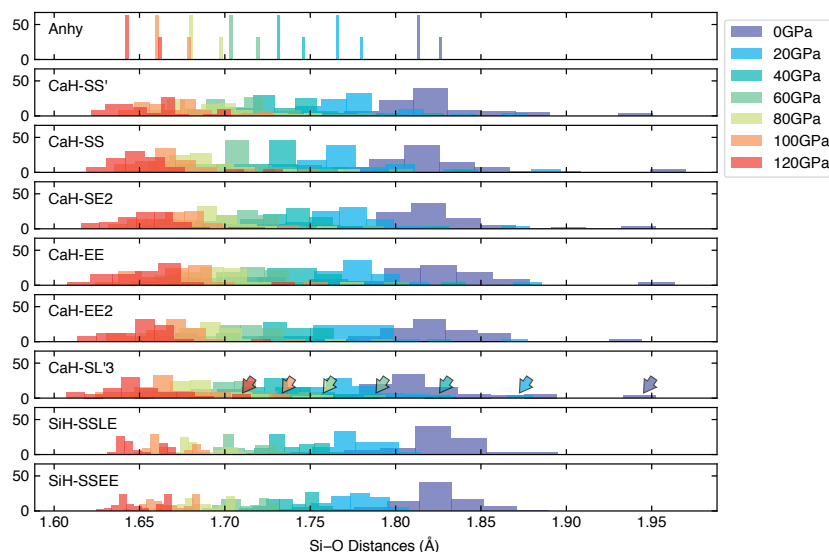


respectively. As a first-order approximation, we estimate the relative formation energies by calculating the ground state of the elemental reference states using the same numerical procedures and PAW-GGA pseudopotentials as in the CaH and SiH models. The diatomic molecules were treated by placing each species in a fixed but slightly distorted cubic cell of dimension ~ 10 Å and optimizing the internal structural coordinates. This procedure yielded bond lengths of 1.229 and 0.750 Å for (triplet) $\text{O}_2(\text{g})$ and $\text{H}_2(\text{g})$, respectively. Calcium and silicon were optimized as face-centered cubic structure and diamond cubic structure yielding cell lengths of 5.53 and 5.44 Å, respectively. Repeating the Ca and Si calculations using $2 \times 2 \times 2$ supercells (cell dimensions ~ 10 – 11 Å) led to a negligible change in their respective energies. Using only the electronic DFT (neglecting vibrational free energy corrections) of the lowest energy models (LL'-90 for CaH and SSLE for SiH), we obtain $\Delta E(\text{CaH}) = -1368$ kJ/mol and $\Delta E(\text{SiH}) = -1351$ kJ/mol, a difference of $\sim 1\%$. This result suggests that at ambient pressure the formation energies of the CaH and SiH hydrous phases are similar.

Infrared-active OH vibrational modes

Chen et al. (2020) reported OH vibration model in infrared (IR) spectra of hydrous CaSiO_3 perovskite. The phase was synthesized from a hydrous starting material in LHDAC at 19 GPa

FIGURE 8. The Si-O distances in the first neighbor. The colors of the bars change from blue to red with pressure. The arrows highlight a small but significant population with very long Si-O distances. Such a population can be found in all CaH structures, while it is absent in the SiH structures. (Color online.)



and 1700 K (Fig. 9c). The documented OH vibrational features were broad (a width of $\sim 200 \text{ cm}^{-1}$) at high pressures between 5 and 19 GPa. At the lowest pressure tested, 0.65 GPa, the OH feature becomes broader ($\sim 300 \text{ cm}^{-1}$) before it disappears at 1 bar where CaSiO_3 perovskite amorphizes.

We conducted calculations for a few selected models in Figures 9a and 9b. Significant differences were found between CaH and SiH models: the OH spectra of CaH structures are much simpler with a peak near 3600 cm^{-1} at 0 GPa, while the spectra of SiH consist of at least two peaks spreading over a wide wavenumber range between 2800 and 3800 cm^{-1} . The most likely reason for the difference is that: while the OH in the dodecahedral sites do not interact with one another because of the large H–H distances (Fig. 5), the OH in the octahedral site has much more complicated bonding environment and interacts with nearby H and O atoms (Figs. 5 and 7).

For the comparison with experimentally reported spectra, we assume that the thermal effects are small between 0 K (for our computation) and 300 K (for the experiments). Our calculation found $100\text{--}200 \text{ cm}^{-1}$ decrease in the wavenumbers of the OH modes during compression from 0 to 30 GPa. Assuming a linear response of mode frequencies to pressure, we estimate a $20\text{--}40 \text{ cm}^{-1}$ decrease in the mode frequency between our calculation (0 GPa) and the OH IR spectra at 5.5 GPa by Chen et al. (2020). Therefore, given the broad nature of the OH vibration observed in experiment, the compressional effect is small.

Our calculation shows that the energy differences between various substitutional configurations are small among the CaH models and among the SiH models at 0 K. In addition, energy differences between the CaH and SiH models are small. Therefore, it is likely that multiples of different configurations coexist at mantle-related conditions (Table 1; Fig. 3). Combination of SiH-SSLL and SiH-SSLE could explain the majority of the intensities observed in the OH region from experiment. These two SiH configurations have lowest energies among the considered SiH configurations at lower pressures (Table 1). As discussed before, SiH-SSLL becomes SiH-SSLE at 20 GPa. The sample by Chen et al. (2020) was synthesized at 19 GPa and 1700 K. Thermal effects could affect the relative stabilities of these two configurations. Therefore, both SiH-SSLL and SiH-SSLE could coexist in the experimentally synthesized sample.

The experimentally measured spectra show much weaker intensity at the frequency region expected for the OH vibration from the CaH configurations. However, our calculation shows much smaller absorbance of the OH modes from CaH compared with SiH (approximately a factor of 10). Therefore, it is feasible that CaH configurations exist in a significant fraction in the hydrous CaSiO_3 perovskite but the intrinsically smaller absorbance from the OH in CaH creates reduced intensities compared with the SiH configurations.

Fu et al. (2019) reported IR active OH vibration from single-crystal $(\text{Mg,Fe})(\text{Al,Si})\text{O}_3$ bridgmanite. They found two major modes at ~ 3220 and $\sim 3470 \text{ cm}^{-1}$ (Fig. 9d). While the modes are broader, wavenumbers of these two modes are similar to those observed in CaSiO_3 perovskite at ~ 3250 and $\sim 3500 \text{ cm}^{-1}$ (Chen et al. 2020). The similarity may support comparison of our calculation on CaSiO_3 perovskite with the experimentally observed OH spectra from bridgmanite. The reported vibra-

tional mode frequencies from bridgmanite are particularly comparable to the two IR modes predicted for the SiH-SSLE configuration (Fig. 7b). Although it is uncertain if the peak at 3700 cm^{-1} in bridgmanite is from the sample rather than noise, if the mode is indeed from the sample, it can be related to OH in the dodecahedral sites. While a greater number of configurations is possible for bridgmanite because of its lower symmetry, our approach here can be used for calculating the energetics of different OH configurations and their IR spectra in bridgmanite in future studies, which will be important for understanding experimental observations regarding H_2O storage in bridgmanite (Murakami et al. 2002; Bolfan-Casanova et al. 2003; Litasov and Ohtani 2003; Fu et al. 2019).

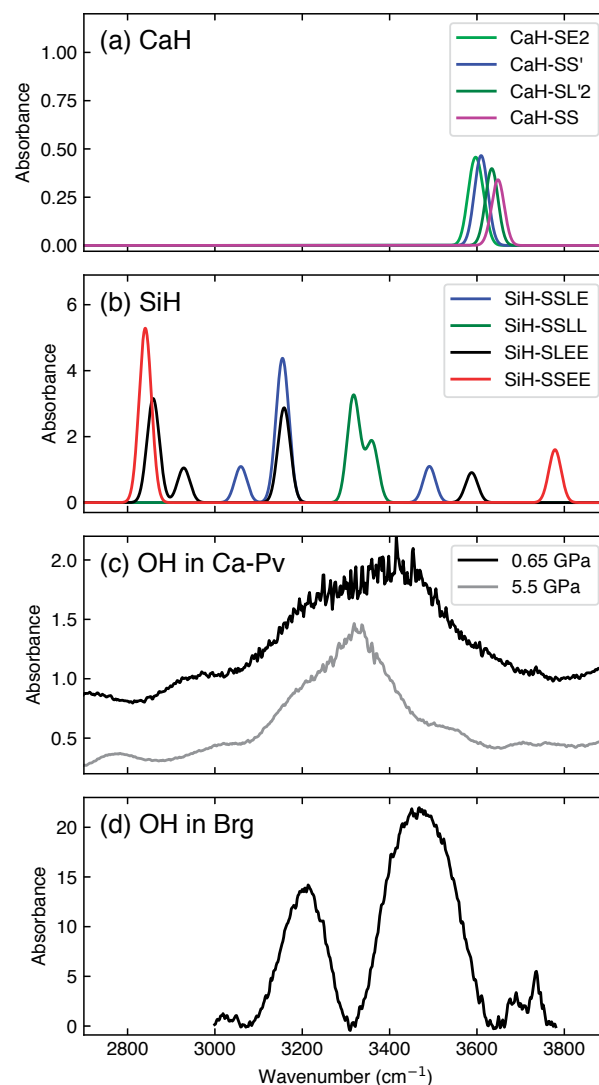


FIGURE 9. Infrared (IR) spectra calculated for OH in (a) the dodecahedral sites (CaH) and (b) the octahedral sites (SiH) in CaSiO_3 perovskite. We also presented experimentally measured IR active OH modes of (c) CaSiO_3 perovskite from Chen et al. (2020) and (d) $(\text{Mg,Fe})(\text{Al,Si})\text{O}_3$ perovskite (bridgmanite) from Fu et al. (2019). (Color online.)

SUMMARY AND IMPLICATIONS

The main findings of our study can be summarized as below:

We consider all the possible dodecahedral ($\text{Ca}^{2+} \rightarrow 2\text{H}^+$; CaH models) and octahedral ($\text{Si}^{2+} \rightarrow 4\text{H}^+$; SiH models) substitution configurations for hydrogen in a tetragonal perovskite lattice of CaSiO_3 . The energy differences among the H configurations in the CaH and the SiH models are sufficiently small that multiples of H configurations will likely coexist at mantle-related pressures and temperatures.

Although distortion in the lattice can play an important role to stabilize diverse H configurations, our calculations suggest that: (1) H-H repulsion, (2) hydrogen bonding, and (3) O-H...O angle are important factors for stabilization of the H configurations.

The impact of the dodecahedral substitutions on the crystal structure is more consistent with the X-ray diffraction observations. All the CaH models predict unit-cell volume decrease by H substitution. The CaH configurations result in much weaker hydrogen bonding. Therefore, O-H covalent bonding remains relatively strong, which introduces severe distortion in the neighboring SiO_6 octahedra. Such enhanced distortion appears to be more consistent with persistence of non-cubic crystal structure of CaSiO_3 perovskite in hydrous environments at high temperatures found in experiments (Chen et al. 2020).

Although some uncertainty remains, the magnitude of distortion predicted by DFT calculations for ~1 wt% H_2O in CaSiO_3 perovskite is consistent with the experimentally reported distortions in the crystal structure, suggesting a few wt% level H_2O storage capacity of CaSiO_3 perovskite.

The infrared-active OH vibrational modes documented in recent experiments on CaSiO_3 perovskite (and bridgmanite) are more consistent with the SiH configurations. The observed large widths of the mode can be explained by the existence of multiple H configurations in the experimentally synthesized hydrous CaSiO_3 perovskite.

The persistence of a non-cubic distortion to mantle temperatures in hydrous CaSiO_3 perovskite opens up an interesting possibility for seismic investigation of hydrous regions in the lower mantle. CaSiO_3 perovskite represents as much as 23 wt% in the subducting basaltic layer (Hirose et al. 2005). The non-cubic distortion in hydrous CaSiO_3 perovskite at mantle temperatures could result in high-elastic anisotropy in the hydrous subducting regions and therefore may open up a possibility to detect such hydrated structures in seismology. In fact, some seismic studies have found anisotropy around the subduction zones in the lower mantle (Chen and Brudzinski 2003; Panning and Romanowicz 2006; Foley and Long 2011).

Astrophysical measurements have found that some stars are rich in Ca compared with the Sun (Hinkel and Unterborn 2018). If terrestrial planets form in the star systems, they would contain more CaSiO_3 perovskite in the mantle, potentially making the lower mantle an important region for H_2O storage. We also showed that the equation of state of CaSiO_3 perovskite can be affected by hydration. Our equations of state (Table 2) can be useful to model the internal structures of such exoplanets combined with measured mass-radius relations.

To further develop a deeper understanding of water storage in the deep mantle, it would be important to explore thermal effects

in ab initio calculations in future studies. The systematic search for a range of possible H configurations we conducted here can be extended to lower symmetric perovskite structured phases in the lower mantle, i.e., bridgmanite, which is important to further advance our knowledge on water storage in the most volumetric layer in the Earth's interior, lower mantle.

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