Post-stishovite transition in hydrous aluminous SiO₂

Koichiro Umemotoa,b,* , Katsuyuki Kawamuraċ , Kei Hiroseb,d,e , Renata M. Wentzcovitchb,f,g

Contents lists available at ScienceDirect

Physics of the Earth and Planetary Interiors

journal homepage: www.elsevier.com/locate/pepi


ARTICLE INFO

Article history:
Received 29 September 2015
Received in revised form 15 March 2016
Accepted 22 March 2016
Available online 29 March 2016

Keywords:
Post-stishovite transition
Hydrous aluminous SiO₂
First principles
Molecular dynamics

ABSTRACT

Lakshtanov et al. (2007) showed that incorporation of aluminum and some water into SiO₂ significantly reduces the post-stishovite transition pressure in SiO₂. This discovery suggested that the ferroelastic post-stishovite transition in subducted MORB crust could be the source of reflectors/scatters with low shear velocities observed in the mid to upper mantle. A few years later, a similar effect was observed in anhydrous Al-bearing silica. In this paper, we show by first principles static calculations and by molecular dynamics using inter-atomic potentials that hydrogen bonds and hydrogen mobility play a crucial role in lowering the post-stishovite transition pressure. A cooperative redistribution of hydrogen atoms is the main mechanism responsible for the transition pressure reduction in hydrous aluminous stishovite. The effect is enhanced by increasing hydrogen concentration. This perspective suggests a potential relationship between the depth of seismic scatterers and the water content in stishovite.

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1. Introduction

Silica (SiO₂) is an abundant component of the Earth’s crust but it is not expected to be present in normal peridotitic mantle. Nevertheless, one of its phase transitions has been implicated as cause of seismological reflectors/scatters observed in the upper mantle (e.g., Kawakatsu and Niu, 1994; Le Stunff et al., 1995; Kaneshima and Helffrich, 1999, 2003, 2009; Vinnik et al., 2001; Niu et al., 2003). Stishovite, the lowest pressure form of SiO₂ containing silicon in octahedral coordination, transforms to CaCl₂-type SiO₂ (post-stishovite transition) at ~ 50 GPa (~1400 km depth) and room temperature (Kingma et al., 1995). It is a second-order ferroelastic transition consisting of an orthorhombic distortion of tetragonal stishovite and displaying large shear modulus softening (Cohen, 1991; Karki et al., 1997; Carpenter et al., 2000; Tsuchiya et al., 2004). The observed seismic heterogeneities may be reconciled with the post-stishovite phase transition in SiO₂ hosted in the subducted MORB crust (e.g., Kaneshima and Helffrich, 1999; Tsuchiya et al., 2004; Hirose et al., 2005) with ~25 mol% SiO₂. Recent high P–T experiments demonstrated that the post-stishovite transition occurs at about 70 GPa along the geotherm in pure SiO₂ (Nomura et al., 2010), accounting for the anomalies approximately at 1500–1800-km depth. Shallower seismic heterogeneities may be attributed to the transition in the Al-bearing SiO₂ phase, with or without water (Lakshtanov et al., 2007; Bolfan-Casanova et al., 2009). Recent first principles calculations of acoustic velocities of stishovite and CaCl₂-type SiO₂ at lower mantle conditions showed surprising results, such as the ΔVp/ΔVφ ~ 2 for this transition at mantle conditions (Yang and Wu, 2014).

Several other possibilities have been suggested to explain mid-lower mantle heterogeneities. The breakdown of phase D (Shieh et al., 1998), a dense hydrous magnesium silicate, into MgSiO₃ perovskite and water could cause hydration of mid-lower mantle around 1500-km depth (Ohtani et al., 2001b; Niu et al., 2003), but it cannot explain the shallower seismic heterogeneities. The tetragonal-cubic transition in CaSiO₃-rich perovskite has also been proposed to cause mid-lower mantle anomalies (Kurashina et al., 2004). However, the phase boundary and the shear velocity discontinuity across the transition are still under debate (Li et al., 2006a, 2006b; Stixrude et al., 2007; Komabayashi et al., 2007). Moreover, such phase transition in Ca-perovskite is expected to occur throughout the entire lower mantle considering the variation in temperature of subducted slabs, while seismic anomalies are found only above 1800-km depth. A spin crossover in Fe³⁺ in Al-bearing

* Corresponding author at: Earth-Life Science Institute, Tokyo Institute of Technology, 2-12-1-IE-12 Ookayama, Meguro-ku, Tokyo 152-8550, Japan.

http://dx.doi.org/10.1016/j.pepi.2016.03.008
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phase D expected to be present in MORB has more recently been proposed also (Chang et al., 2013). Iron spin crossovers in lower mantle minerals occur in broad pressure ranges (Badro et al., 2003, 2004; Tsujiya et al., 2006; Lin et al., 2007; Wentzcovitch et al., 2009) and their effects on seismic velocities seem to reach a maximum between 1200 km and 1800 km depth (Wentzcovitch et al., 2009; Cataldi et al., 2010; Hsu et al., 2011; Wu and Wentzcovitch, 2014), which correlates well with the depth range of observed scatterers. However, spin crossovers affect most strongly bulk and longitudinal velocities (Marquardt et al., 2009; Wu et al., 2013). Their effect on shear velocities is still debated (Crowhurst et al., 2008; Antonangeli et al., 2011).

In this paper we report a computational study of the post-stishovite transition in anhydrous and hydrous aluminous SiO₂. Our goal is to understand the roles that alumina and water play separately on the transition and implications of seismological observations in light of these results. First we investigate by first principles the nature of the aluminous defect, with and without hydrogen, in supercells containing up to 163 atoms. We uncover a cooperative effect associated with hydrogen bonds (H-bonds) and hydrogen motion. After characterizing these defects, we perform large-scale molecular dynamics simulations using interatomic potentials reproducing experimental conditions more closely.

2. Computational methods

2.1. First-principles calculations

These density functional calculations were performed using the PBE-type generalized gradient approximation (GGA) (Perdew et al., 1996). We have used Vanderbilt pseudopotentials (Vanderbilt, 1990) for all elements. We used the same cut-off radius for angular momenta for each element: 1.6, 2.0,1.4, and 0.6 a.u for Si, Al, O, and H, respectively. The plane-wave energy cut-off was 40 Ry. k-point meshes were 4 × 4 × 6, 2 × 2 × 4, 1 × 2 × 4, 2 × 2 × 2 and 2 × 2 × 2 for 1 × 1 × 1 (i.e., pure stishovite), 2 × 2 × 2, 4 × 2 × 2, 2 × 2 × 2, 2 × 3 × 2, and 3 × 3 × 3 supercells, respectively. Total energies converged to less than 1 mJ/atom. Structural optimizations at arbitrary target pressures were performed using variable cell shape molecular dynamics (Wentzcovitch, 1991). To determine the phase boundary of the post-stishovite transition in pure SiO₂, quasi-harmonic approximation was applied, combined with phonon frequencies calculated by density-functional-perturbation theory (Giannozzi et al., 1991; Baroni et al., 2001). All first-principles calculations were performed by using the Quantum ESPRESSO software distribution (Giannozzi et al., 2009).

2.2. Molecular dynamics (MD) simulations

N-P-T ensemble MD simulations were conducted at temperatures of 300, 500, 700, 900, 1100, 1300, and 1500 K at 0, 10, 20, 30, 40, 50, and 60 GPa using 8 × 8 × 12 supercells (4704 atoms) containing 6.25% AlOOH. Two-body interatomic potentials were used. Functional forms for these two-body interatomic potentials were adopted from Nakano et al. (2003) which investigated sheet silicates with water and solutions. Appendix A discusses the validity of the model potentials along with the parameters (Table 1) used in the present study. The latter were further modified to reproduce structural behaviors of systems comprising silicon, aluminum, oxygen and hydrogen atoms. Variable cell shape simulations were allowed to evolve and equilibrate for 0.2 ns to achieve thermodynamic equilibrium. Hydrogen motion was monitored for 0.01 ns after cell equilibrations in terms of mean square displacements (MSDs). MD simulations were performed using the MMDORTO/MXDTRICL software developed by Kawamura et al. (available at http://kats-labo.jimdo.com/mxdorto-mxdtricl/). This software has been successfully applied to sheet silicates (Sakuma et al., 2011), zeolites and molten salts (Uozumi et al., 2015), silicate melts (Noritake et al., 2015) and so on.

3. Results and discussion

3.1. First principles defect calculations

3.1.1. Hydrous defect (SiO₂ ↔ AlOOH)

First, we address the combined effect of aluminum and hydrogen by means of SiO₂ ↔ AlOOH substitutions. Pure AlOOH exists in the CaCl₂-type phase, the δ-AlOOH phase (Suzuki et al., 2000; Ohtani et al., 2001), which is highly soluble in stishovite (Pawley et al., 1993; Chung and Kagi, 2002). Calculations were performed in 2 × 2 × 2 (49 atoms) and 3 × 3 × 3 (163 atoms) supercells with one AlOOH unit/cell (6.25 mol% 6.24 wt% AlOOH or 5.30 wt% Al₂O₃ + 0.94 wt% H₂O) and 1.85 mol% (1.85 wt% AlOOH or 1.57 wt% Al₂O₃ + 0.28 wt% H₂O), respectively. Possible defect configurations are illustrated in Fig. 1. There are twelve hydrogen sites grouped in two symmetry related sets in the vicinity of an Al-octahedron: a fourfold degenerate site (H₁) and an eightfold degenerate (H₂). H₁ and H₂ hydrogens are bonded to apical and equatorial oxygens of the Al-octahedron, respectively. H₂ hydrogens are more stable than H₁ s. Previously, H₂ hydrogens were reported to be unstable in LDA calculations (Panero and Stixrude, 2004). The enthalpy difference between these two types of hydrogens is ~0.010 Ry at 0 GPa in the 2 × 2 × 2 supercell and decreases to ~0.006 Ry at 50 GPa. Their relative populations are

\[
N₂/N₁ = \exp \left[ -\frac{(H₂ - H₁) - k_B T \ln 2}{k_B T} \right]
\]

where H₁ and H₂ are enthalpies of H₁ and H₂ hydrogen types. The (k_BT) factor appears because H₂ sites are twice as abundant as the H₁ sites. For instance, at 1000 K, N₁ ~ 9% and N₂ ~ 91% at 0 GPa, and N₁ ~ 17% and N₂ ~ 83% at 50 GPa. These calculations reveal a remarkably strong and concentration-dependent “chemical” effect of hydrogen on the post-stishovite transition (Fig. 2). Stishovite supercells with one...

<table>
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<tr>
<th>Atom</th>
<th>w (10⁻³ kg mol⁻¹)</th>
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<th>a (nm)</th>
<th>b (nm)</th>
<th>c (kJ/mol) Å nm⁻³</th>
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<td>β₁ (nm⁻¹)</td>
<td>D₂ (kJ mol⁻¹)</td>
<td>β₂ (nm⁻¹)</td>
<td>D₃ (kJ mol⁻¹)</td>
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<td>O–H</td>
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<td>74.0</td>
<td>-3725.6</td>
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AlOOH unit are orthorhombic even at 0 GPa. The distortion increases with pressure, and its magnitude depends on the hydrogen site/type and concentration, the distortion increasing with the latter. The strong distortion is caused by a hydrogen bond (H-bond) formed with the oxygen across the interstitial site. Depending on the hydrogen position, the H-bond aligns more along the \( a \) or the \( b \) axis, which determines whether the distortion produces \( a > b \) or \( a < b \) (Fig. 1(B)). The orthorhombic symmetry further splits \( H_1 \) and \( H_2 \) hydrogens into two sets each, twofold \( H_{11} \) and \( H_{12} \), and fourfold \( H_{21} \) and \( H_{22} \). \( H_1 \) and \( H_2 \), hydrogens make \( a > b \), while \( H_{11} \) and \( H_{21} \) make \( a < b \). This result is a consequence of the long range order and cooperative alignment of H-bonds in calculations containing a single AlOOH unit per supercell. Therefore, it is apparent that AlOOH-bearing stishovite should have hydrogens randomly distributed, mostly in \( H_2 \) sites, in a way that stresses caused by one H-bond are opposed and canceled by stresses caused by all others, keeping the structure in the averaged undistorted tetragonal structure.

To illustrate this point, we prepared \( 4 \times 2 \times 2 \) supercells with two AlOOH units and two H-bonds. Two different configurations were generated: (i) one \( H_{21} \) and one \( H_{22} \). This configuration keeps \( a \approx b \) and is referred to as tetragonal. These hydrogens individually promote opposing distortions with canceling effects. Beyond 50 GPa, this structure undergoes the usual orthorhombic distortion, similar to defect-free stishovite; and (ii) two \( H_{22} \). This configuration produces \( a < b \), the orthorhombic \( CaCl_2 \)-type structure. Stresses caused by these H-bonds add coherently resulting in a large distortion even at 0 GPa. The orthorhombic structure is more stable at all pressures in these static calculations. The equilibrium lattice parameters \( a \) and \( b \) of these two configurations are shown in Fig. 3. However, as will be shown later, upon warming, configuration entropy contributes to the stabilization of the tetragonal structure, because of the higher number of hydrogen configurations in the tetragonal structure. Qualitatively, our approximate treatment of configuration entropy indicates that increasing temperature favors the tetragonal structure over the orthorhombic one producing a positive Clapeyron slope (See Appendix B) and the post-stishovite transition in AlOOH-bearing SiO\(_2\) is accompanied by a redistribution of hydrogens. Therefore, the mechanism of the hydrous post-stishovite transition is different from that in pure stishovite; the post-stishovite transition induced by hydrogen redistribution is a first-order transition accompanied by an entropy discontinuity (see Section 3.3).

### 3.1.2. Anhydrous defect (2SiO\(_2\) ↔ Al\(_2\)O\(_3\))

We also investigated effects of incorporation of Al\(_2\)O\(_3\). We replaced 2SiO\(_2\) with Al\(_2\)O\(_3\). This defect consists of two Al\(_6\) and one V\(_7\) (assigned charges are only formal), i.e., the anhydrous defect. We consider two defect configurations: (i) two corner-sharing, and (ii) two edge-sharing Al-octahedra with an oxygen vacancy in between (see Fig. 4). We carried out static calculations for both types in \( 2 \times 2 \times 4 \) supercells with 95 atoms. At 0 GPa, the edge-sharing defect has lower enthalpy, but pressure stabilizes the corner sharing defect beyond 40 GPa. Supercells with both types of defects display an orthorhombic distortion beyond 50 GPa, similar to aluminum-free stishovite (Fig. 4). Therefore, the post-stishovite transition is not affected by the presence of Al\(_2\)O\(_3\). This conclusion is consistent with that of a previous calculation (Panero, 2006). Our results of hydrous and anhydrous systems reveal that the presence of hydrogen is crucial in shifting the transition pressure. This finding does not support conclusions from recent \textit{in situ} X-ray diffraction experiments with a laser-heated diamond-anvil cell on the post-stishovite transition on the anhydrous Al-bearing phase (Bolfan-Casanova et al., 2009). This experiment observed a substantial decrease in the transition pressure with the addition of

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**Fig. 1.** (A) Possible equilibrium sites of hydrogen in aluminous stishovite. White spheres represent possible hydrogen sites. (B) Resulting orthorhombic distortions depending on hydrogen bond orientations.

**Fig. 2.** Pressure dependence of the lattice constants ratio, \( b/a \), calculated by first principles for \( 2 \times 2 \times 2 \) (6.25 mol% AlOOH) and \( 3 \times 3 \times 3 \) (1.85 mol% AlOOH) supercells of SiO\(_2\) with one AlOOH. Inset shows hydrogen positions.

**Fig. 3.** Lattice constants, \( a \) and \( b \), calculated by first principles for tetragonal and orthorhombic structures for \( 4 \times 2 \times 2 \) supercells with 98 atoms containing two hydrogen bonds per supercell. The tetragonal phase contains one \( H_{21} \) and one \( H_{22} \) hydrogens. The orthorhombic phase contains two \( H_{22} \) hydrogens. See Fig. 1 for the definition of \( H_{21} \) and \( H_{22} \).
4 wt.% Al₂O₃. There might be two possible sources of this discrepancy between theoretical and experimental studies: (1) a trace amount of water, which might have remained even after careful experimental treatments, would play a crucial role in the transition or (2) more complex atomistic phenomena, so far not identified by theoretical studies, is responsible for the transition pressure shift in the absence of water.

### 3.2. Molecular dynamics simulations

The above first-principles results indicate that, superposed to the ferroelastic post-stishovite transition displaying shear modulus softening, there is a strong chemical effect caused by H-bonds. The latter decreases the transition pressure by an amount that depends on hydrogen concentration and temperature (i.e., hydrogen configuration). Throughout the hydrous post-stishovite transition, the hydrogen configuration must change, i.e., hydrogen ions must be mobile to explore configuration space. If not, hydrogen might not affect the post-stishovite transition boundary.

To investigate hydrogen dynamics in the post-stishovite transition, we performed MD simulations in 8×12 supercells (4704 atoms). The goal is to confirm the correlation between structural distortion and hydrogen motion. The initial configurations consisted of 96 uniformly distributed aluminum atoms with hydrogen atoms randomly distributed among the twelve sites surrounding each aluminum octahedron (6.25 mol% of AlOOH).

Fig. 5 shows hydrogen trajectories and the lattice constant ratio, b/a, in some of these MD runs. Below ~500 K, hydrogen motion is severely suppressed. The effect of AlOOH is negligible, and the post-stishovite transition pressure is ~50–60 GPa (Figs. 5(A) and 6), essentially the same as in pure silica (see Fig. 6). Suppression of hydrogen motion does not change the transition pressure or the nature of the post-stishovite transition at low temperatures if one starts in the tetragonal phase. At these low temperatures, the transition is induced by the normal mechanical/ dynamical instability observed in stishovite. As temperature increases, hydrogen mobility also increases. Short-range hopping, mostly between sites surrounding a single oxygen octahedron, is followed by the orthorhombic structural distortion at ~40–50 GPa. This is thermal “annealing” of the metastable structure, not a thermodynamic phase transition. Hydrogen ions were initially “trapped” in the tetragonal configuration and now find their way to more stable sites in the orthorhombic structure lowering the free energy. At ~900 K, this effect is strongest and this type of hydrogen hopping is more frequent. These orthorhombic distortions, although not severe, occur at pressures as low as ~20–30 GPa (Figs. 5(B) and 6). At 1100 ~ 1300 K, the structure remains tetragonal to higher pressures (Figs. 5(C) and 6). This is the real pressure-induced hydrous post-stishovite transition. This is a first order phase transition involving redistribution of hydrogens. At 1500 K, the transition pressure is ~50–60 GPa (Figs. 5(D) and 6). At this temperature, there is no significant effect of hydrogens and the normal ferroelastic post-stishovite transition takes place (Fig. 5(D)). Hydrogen motion no longer plays a role in assisting the phase transition that is now driven by the elastic instability. Hydrogen atoms necessarily redistribute with structural distortion and this transition is now accompanied by entropy and volume change as in a normal first order transition.

The nature of hydrogen motion is illustrated in Fig. 7 showing MSDs (Fig. 7A) and the trajectory of one hydrogen at 1300 K and 60 GPa (Fig. 7B). At 1300 K, hydrogen motion is significant, especially along the c axis. From the trajectory of one hydrogen (Fig. 7/B), we can see that hydrogen ions hop around possible sites shown in Fig. 1, while displaying more obvious diffusive behavior along the c axis. This is the type of motion that helps the entropic stabilization of the tetragonal phase.

Although we only report results of few simulations, similar runs starting from distinct but equivalent configurations produced completely similar results (see right panels in Fig. 5). There are large uncertainties in transition pressures caused by the initial atomic configuration in the MD runs (see error bars in Fig. 6). Therefore, one must not take transition pressures and temperatures literally, especially at low temperatures. Besides, aluminum is uniformly distributed in the simulation cells instead of randomly distributed. Our goal here is to investigate the relationship between hydrogen distribution/motion and structural distortions. Nevertheless, some lessons learned apply to interpretation of experiments. For instance, tetragonal hydrous stishovite samples at low temperatures and pressures might be metastable. The tetragonal phase can exist metastably because of the first-order nature of the hydrous post-stishovite (see Section 3.3). Upon initial slow moderate warming and cooling cycles, hydrous stishovite might be annealed into a thermodynamically stable orthorhombic phase at low temperatures. In hydrous aluminum stishovite, further aluminum disorder – not considered here – might help to stabilize the tetragonal phase. But clearly, if hydrogen motion is suppressed at low temperatures, AlOOH incorporation should not affect the transition pressure significantly. Change in the post-stishovite transition pressure implies that hydrogen is mobile.

At high temperatures where hydrogen ions are mobile, we can also anticipate that the post-stishovite transition in hydrous aluminum stishovite will have a larger Clapeyron slope than the transition in pure SiO₂ (Fig. 6), i.e., ~6 MPa/K (Tsuchiya et al., 2004). In addition to the decrease in vibrational entropy across the regular post-stishovite transition in silica, there is additional reduction in hydrogen configuration entropy. Surely the Clapeyron slope of the hydrous post-stishovite transition should depend monotonically on the AlOOH concentration. Summarized results of MD simulations on a supercell containing 6.25 mol% AlOOH reported in Fig. 6 suggest a Clapeyron slope of ~50 ± 30 MPa/K. This is much steeper than that of AlOOH-free stishovite, because there is an additional effect of hydrogen configuration entropy (see Appendix B).

### 3.3. First-order versus second-order transition

The post-stishovite transition in pure SiO₂ has been well investigated (Cohen, 1991; Karki et al., 1997; Carpenter et al., 2000;
Beyond the transition pressure, the zone-center B1g soft mode induces tetrahedral rotations. Correspondingly, one of the Born stability criteria breaks down \((c_{11}/c_{12} < 0)\), leading to a mechanical instability. This instability drives the tetragonal to orthorhombic transition. Across this transition, lattice constants change continuously and there is (almost) no volume or entropy discontinuities. This is a second-order ferroelastic transition. Also, in Al-bearing SiO2, i.e., without reordering of oxygen vacancies and without hydrogen ions, the post-stishovite transition occurs when the Born stability criteria breaks down (Figs. 4 and 8); this is also a second-order transition.

However, the presence of mobile hydrogen changes the nature of this transition. Below \(~500\) K the free energy of the orthorhombic phase is always lower than that of the tetragonal phase (see Appendix B). Above \(~500\) K, hydrogen configuration entropy contributes further to the stabilization of the tetragonal phase with respect to the orthorhombic phase. Under pressure, redistribution of hydrogens further helps to induce the post-stishovite transition. Now lattice constants \(a\) and \(b\) change discontinuously (e.g., see Fig. 3) at the transition pressure that is lower than that of the ferroelastic transition in pure SiO2. But the Born stability criteria, \(c_{11} - c_{12}\), of the tetragonal phase does not break down until \(~50\) GPa (Fig. 8). The presence of water hardly affects this criterion. All these indicators point to a first-order post-stishovite transition in the presence of water, in contrast to the second-order transition in anhydrous stishovite.

**Fig. 5.** (Left and middle panels) Hydrogen trajectories (represented by black lines) in MD simulations at 60 GPa viewed along the \(c\) axis (left) and \(b\) axis (middle). Small light blue and purple spheres denote silicon and aluminum respectively. Large yellow spheres denote oxygens. (Right panels) Pressure dependence of \(b/a\) for three MD simulations containing 4704 atoms starting from three different configurations containing 96 aluminum atoms uniformly distributed and hydrogens in different randomly chosen configurations. Deviation of \(b/a\) from 1 in this figure is smaller than that in Fig. 2, it is because of hydrogen distribution. In the MD simulation, there are 96 hydrogen atoms. Even in orthorhombic phase, all hydrogen atoms not necessarily induce the orthorhombic distortion along the same direction; minor part of hydrogen atoms induce the distortion along the opposite direction. Hence, there is cancelation. On the other hand, in the first principles calculation in Fig. 2, only one hydrogen atom was put in the cell and no cancelation effect occurred. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Tsuchiya et al., 2004; Yang and Wu, 2014.) Beyond the transition pressure, the zone-center B1g soft mode induces tetrahedral rotations. Correspondingly, one of the Born stability criteria breaks down \((c_{11}/c_{12} < 0)\), leading to a mechanical instability. This instability drives the tetragonal to orthorhombic transition. Across this transition, lattice constants change continuously and there is (almost) no volume or entropy discontinuities. This is a second order ferroelastic transition. Also, in Al-bearing SiO2, i.e., without reordering of oxygen vacancies and without hydrogen ions, the post-stishovite transition occurs when the Born stability criteria breaks down (Figs. 4 and 8); this is also a second-order transition.
Because of the first-order transition, hysteresis is possible experimentally and in MD simulations, and the tetragonal phase may remain metastable in the stability field of the orthorhombic phase at low temperatures where hydrogen motion is severely suppressed. This is what is happening around and below \( \sim 500 \text{ K} \) in Figs. 5 and 6. The post-stishovite transition under compression occurs not by hydrogen redistribution at this temperature but by the breakdown of a Born stability criterion, \( c_{11}/c_{12} \) (Fig. 8), at \( \sim 50 \text{ GPa} \). If the transformation occurs without hydrogen rearrangement, the transition is still a second order ferroelastic transition.

This insight into the nature of the hydrous post-stishovite transition might be relevant for experimental investigations. Experiments in Lakhtanov et al. (2007) indicated that the sample at ambient condition was tetragonal. This might seem inconsistent with our qualitative results (see Appendix B suggesting that the tetragonal phase might be metastable at ambient condition). However, the experimental sample was prepared at 20 GPa and 1800 °C. At these conditions the sample should be tetragonal (see Fig. 6). After quenching to ambient conditions the tetragonal sample might have been kept metastable because of structural hysteresis. Unless hydrogen is mobile, the required rearrangement to induce the hydrous post-stishovite transition does not take place and the transition remains ferroelastic in nature. In the same work the sample was annealed beyond 20 GPa to relax deviatoric stresses in the sample. Our study suggests that if the sample had not been annealed, the second-order transition might have been
observed at ~50 GPa. In summary, annealing should be critical in the
determination of the hydrous post-stishovite transition boundary.

3.4. Further insights from elasticity

Fig. 9 shows acoustic velocities calculated using the tetragonal
$4 \times 2 \times 2$ supercell (6.25 mol% of AIOOH). Results are compared
with velocities obtained by Brillouin scattering for samples con-
taining 6.07 wt% of Al$_2$O$_3$ and 0.24 wt% H$_2$O (Lakshtanov et al.,
2007). The dip of acoustic velocity reported by experiments and
by high temperature calculations (Yang and Wu, 2014) is well
reproduced. Correspondingly, the calculated shear modulus has a
dip across the transition. The underestimated velocity in these cal-
culations originates primarily in the use of GGA, which overesti-
mates volume and underestimates elastic properties. The use of
GGA was preferred because of the presence of hydrogen bonds
and their importance in this transition. The level of agreement with
measured velocities is similar to other GGA calculations, despite
the static nature of the hydrogen ions. Therefore, velocities of pure
and hydrous aluminium stishovite do not appear dramatically dif-
fent, but the hydrous supercell distorts more readily under pres-
sure. This behavior suggests that in Brillouin experiments,
hydrogen motion at room temperature was not vigorous, except
at the transition, where hydrogen configurations must change with
change of symmetry if the transition pressure is affected. Experi-
mentally, the transformation occurs at 25 GPa, as seen in Fig. 9.

These calculations suggest that hydrogen possibly affects con-
siderably the elastic properties of stishovite at temperatures where
hydrogen is mobile. Small deformations of the tetragonal cell
reduce degeneracies of hydrogen configurations, changing the
equilibrium populations of hydrogen sites. If the time frame of
the applied load is comparable to hydrogen relaxation times, rear-
angement of hydrogen ions will take place, which will signifi-
cantly affect elastic properties. Although seismic waves produce
small stresses, their periods are large enough (>1 s) and should
allow hydrogen relaxation into equilibrium configurations at man-
tle temperatures. Such anelastic deformation, termed the Snoek
relaxation, is well-documented for bcc metals containing a small
concentration of small, highly mobile interstitial solute atoms
including H, C, N or O (Blanter et al., 2007). One may expect anelas-
tic deformation in hydrous silica. Let us consider tetragonal
AIOOH-bearing SiO$_2$. In the tetragonal phase, hydrogen atoms are
randomly distributed over possible H$_1$ and H$_2$ sites; probability
on H$_2$ sites should be higher than that on H$_1$, since H$_2$ sites
are energetically favored than H$_1$ sites (Section 3.1.1). When a cer-
tain stress is applied along $a$ or $b$ axes, it induces an orthorhombic
strain and hydrogen occupation of H$_1$ and H$_2$ sites should change
since energetic degeneracy of both H$_1$ and H$_2$ sites are lifted in
the orthorhombic phase. Such redistribution of hydrogen atoms
should produce additional strain leading to a strong cooperative
effect on the post-stishovite transition. This anelastic effect is
expected to occur at high temperatures when hydrogen is mobile and
if the time scale of applied stress is comparable to relaxation
time for hydrogen hopping. After the stress is removed, the occu-
pancy of H$_1$ and H$_2$ sites by hydrogen should go back to the origi-
nal one corresponding to the tetragonal phase. This type of
relaxation is expected to play a role in elastic/seismic properties.
Calculation of the relaxed elastic moduli is beyond the scope of this
work and is left for future theoretical/experimental studies. If
anelastic deformation occur in hydrous silica, these relaxed moduli
should be considerably reduced.

4. Geophysical implications

So far, several possible origins for seismic reflectors/scatterers
observed in upper to middle lower mantle (800–1500-km depth)
have been proposed: the breakdown of phase D, the tetragonal-
cubic phase transition of Ca-perovskite, the post-stishovite tran-
sition in pure SiO$_2$, and the spin transition if Fe$^{3+}$ in phase D. Our
results suggest that the hydrous post-stishovite transition is also
a likely candidate. The depth/pressure range of the scatterers
might be consequence of variable H$_2$O in stishovite in MORB crusts
subducted into the lower mantle. While the role of stishovite in
carrying water into the lower mantle has been stressed (Litavov
and Ohtani, 2005), the amount of H$_2$O incorporated in Al-bearing
stishovite has remained controversial. The solubility of Al$_2$O$_3$
strongly depends on temperature and is possibly <1 wt% below
1400 K as indicated by (Ono et al., 2002), which limits the amount
of H$_2$O transported by stishovite (Lakshtanov et al., 2007; Ono
et al., 2002). Nevertheless, this study indicates that in hydrous
stishovite a phase transition could occur in the upper to middle
layers of the lower mantle and the transition pressure should
depend on the H$_2$O content. Shear velocity anomalies accompa-
ing this transition could be enhanced by relaxation of hydrogen
positions at high temperatures.

5. Summary

We have shown that hydrogen affects the ferroelastic post-
stishovite transition pressure in two major ways: (1) by changing
equilibrium states, i.e., the phase boundary, and (2) by introducing
extra kinetic effects. As far as equilibrium state is concerned,
H-bond formation in hydrous aluminium stishovite can signifi-
cantly reduce the transition pressure of the post-stishovite
transition by cooperatively inducing an orthorhombic distortion
at low temperatures. At high temperatures, hydrogen configuration
entropy should further stabilize the tetragonal structure. This
results in an overall increase in Clapeyron slope. As far as kinetic
effects are concerned, hydrogen mobility is key for finding equilib-
rium states, i.e., mapping the phase diagram. The MD simulations
in this paper display both equilibrium and kinetics effects simultane-
ously. In addition, it does not treat hydrogen motion quantum
mechanically, further suppressing hydrogen motion. Equilibrium and kinetics effects combined produce a non-equilibrium MD phase boundary at low temperatures that is completely biased towards the initial state, a tetragonal one. Suppression of hydrogen motion does not affect the post-stishovite transition pressure at low temperatures, if one starts in the tetragonal structure. At higher temperatures hydrogen mobility allowed ground states to be more clearly mapped in these simulations, revealing the anticipated phase diagram with a larger Clapeyron slope.

This understanding also points to the motion of hydrogen ions as an important source of anelasticity and, hence, reduction, dispersion, and attenuation of seismic waves in hydrous aluminous stishovite. Although the real system is far more complex than those simulated and more complex atomistic phenomena cannot be ruled out, our results suggest that Al₂O₃ alone does not affect the post-stishovite transition pressure at low temperatures, if one starts in the tetragonal structure. At higher temperatures hydrogen mobility allowed ground states to be more clearly identified, significant, and concentration dependent.

Acknowledgments

The authors thank David Kohlstedt, Justin Revenaugh, and George Helffrich for useful discussions. This work was supported by NSF under Grants EAR-1161023 and EAR-1348066. Computations were performed at the Minnesota Supercomputing Institute (MSI) and in the Blue Waters system at NCSA.

Appendix A. Validity of the model potential used by the MD simulations

In order to check the validity of the model potential whose parameters are listed in Table 1, here we compare some results from MD simulations with those by first principles. In Fig. 6, the post-stishovite transition pressures in pure SiO₂ obtained by MD simulations are shown by black rectangles. They agree very well with first-principles QHA calculations (black line in Fig. 6) despite the difference between classical and quantum approaches to atomic motion. Fig. 10 shows lattice constants of tetragonal AlOOH-bearing SiO₂ by the MD simulation at 300 K and by static first-principles calculations. Lattice constants by the MD simulation are smaller than those by first principles. It is because GGA tends to overestimate lattice constants compared to experiments. Also, first principles results in Fig. 10 are by static calculations, i.e., without phonon effects. Nevertheless, the model potential used by the MD simulation reproduces the overall pressure dependence of structural properties by first principles in AlOOH-bearing SiO₂.

Appendix B. Approximate treatment of effects of hydrogen configurations

First-principles calculations of the effect of hydrogen configurations were conducted on 4 × 2 × 2 supercells with two AlOOH units (i.e., two H-bonds) in order to generate both tetragonal and orthorhombic structures. The supercells are tetragonal when two hydrogen ions are placed on H₂₁ and H₂₂ sites (see Fig. 1) or orthorhombic when they are both on H₂₁ or H₂₂. Therefore, the number of hydrogen configurations in the tetragonal structure is larger than in the orthorhombic structure. Similarly, configuration entropy in the tetragonal structure is higher than in the orthorhombic structure. A quantitative estimate of the configuration entropy should start from the partition function sampling all possible hydrogen configurations for supercells which should be much larger than the supercells used in the present study. This is unfeasible by first principles. Instead, we quantitatively address configuration entropy in the relatively small 4 × 2 × 2 supercells in the following way: around each Al-octahedron, there are four H₂₁ or H₂₂ sites. In the tetragonal structure, two hydrogens are distributed randomly over these sites. There are eight possible sites for each hydrogen around each Al-octahedron, therefore, there are 64 H configurations for a cell with two Al ions. In contrast, in the orthorhombic structure two hydrogens are distributed randomly over H₂₁ or H₂₂ sites only (leading to a > b or a < b), resulting in 4 × 4, i.e., 16 configurations. In this way, configuration entropy is estimated to be approximately \(k_B \ln 64\) and \(k_B \ln 16\) for tetragonal and orthorhombic structures, respectively (\(k_B\) is the Boltzmann constant). With these entropies, we can estimate Gibbs free energies for tetragonal and orthorhombic phases at finite temperatures:

\[ G_{\text{tetra}}(P,T) = H_{\text{tetra}}(P) - T S_{\text{tetra}}(P), \]

where \(H\) is enthalpy for each structure. At 0 K, Gibbs free energy is equivalent to enthalpy. Differences in Gibbs free energies between tetragonal and orthorhombic structures at several temperatures (\(AG = G_{\text{ortho}} - G_{\text{tetra}}\)) are shown in Fig. 11. Below approximately 300 K, \(AG\) is always negative and the orthorhombic phase is stable.

![Fig. 10. Pressure dependencies of lattice constants for tetragonal structure of SiO₂ with 6.25 mol% AlOOH by first principles in the 4 × 2 × 2 supercell (filled circles), as shown/discussed in Fig. 3, and the MD simulations in the 8 × 8 × 12 supercell (open circles), where hydrogen configuration is fully disordered.](image1)

![Fig. 11. First-principles Gibbs free energy difference between two configurations (4 × 2 × 2 supercells with 98 atoms) containing two hydrogen bonds per supercell. The tetragonal phase contains one H₂₁ and one H₂₂ hydrogens. The orthorhombic phase contains two H₂₂ hydrogens.](image2)
at all pressures. Above ~300 K AG is positive below a critical pressure and the post-stishovite transformation takes place at high pressures. Transition pressures are ~6, 24, 32, and 38 GPa at 500, 1000, 1500, and 2000 K, respectively. The post-stishovite transition has positive Clapeyron slope. This positive slope is further enhanced because of the extra reduction of entropy caused by hydrogen redistribution. Again, we emphasize that the above treatment of configuration entropy is just qualitative. Also we do not take into account vibrational effects which are important at finite temperatures. Therefore, the temperature dependence of the transition pressure, at which AG = 0, is only qualitatively accurate.

References


