Atomistic Mechanism of Al Substitution Effects on the Pseudo-Proper Typed Ferroelastic Post-stishovite Transition by High-Pressure Single-Crystal X-Ray Diffraction

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Abstract

Influence of the Al substitution on the elastic properties of stishovite and its transition to post-stishovite is of great importance in comprehending the seismic wave velocities of subducted mid-ocean ridge basalt (MORB) within the mantle transition zone and the lower mantle. However, Al effects on the transition mechanism and elasticity remain much debated due to the lack of reliable information about atomic positions and crystal structures across the post-stishovite transition. Here synchrotron single-crystal X-ray diffraction (SCXRD) has been performed on Al1.3-SiO_2 (1.3 mol% Al) and Al2.1-SiO_2 (2.1 mol% Al) crystals in diamond anvil cells with Boehler-Almax designed anvils up to ~41 GPa at 300 K. Refinements of SCXRD spectra show that a phase transition from stishovite (space group $P4_2/mnm$; No. 136) to $CaCl_2$-typed post-stishovite (space group *Pnnm*; No. 58) occurs between 20.4-22.5 GPa in the Al1.3-SiO_2 crystal and 14.3-16.4 GPa in the Al2.1-SiO_2 crystal. The post-stishovite transition is accompanied by splitting of O coordinates, crossover of apical and equatorial (Si,Al)-O bond lengths, and vanishing of (Si,Al)O_6 octahedral distortion. The Al substitution in stishovite results in a faster decrease in the O coordinate, stiffer apical but softer equatorial (Si,Al)-O bond, and a less distorted (Si,Al)O_6 octahedron under pressure. The correlation between the crossover of the

(Si,Al)-O bond lengths and post-stishovite transition, together with complimentary optic modes and spontaneous strains, support the notion that the Al1.3-SiO_2 and Al2.1-SiO_2 crystals undergo a pseudo-proper typed ferroelastic post-stishovite transition. The reduction in elastic moduli and sound velocities with the Al substitution in stishovite may be attributed to decreased O coordinates, softer apical (Si,Al)-O3 bonds, and less distorted (Si,Al)O_6 octahedra at high pressure. Correlation between elasticity from Landau modeling and (Si,Al)-O bond length difference from this study reveals that at a constant degree of (Si,Al)O_6 octahedral distortion, the Al substitution results in lower elastic moduli and sound velocities, which in turn aids in our understanding of seismic properties of MORB in the deep mantle.

Keywords: Al-bearing stishovite, single-crystal X-ray diffraction, pseudo-proper typed ferroelastic transition, post-stishovite, lower-mantle seismic scatterers, elasticity

Running title: Atomistic Mechanism of Aluminum-Bearing Post-Stishovite Transition

Introduction

Stishovite is expected to be an abundant component in subducted mid-ocean ridge basalt (MORB) in the mantle transition zone and the lower mantle (Hirose et al. 1999; Litasov and Ohtani 2005; Ishii et al. 2019). Previous experimental studies have shown that in a MORB composition, stishovite can accommodate up to 4 mol% Al it its structure mainly through charge-coupled substitutions of $Al^{3+} + H^{+} = Si^{4+}$ and $2Al^{3+} + V_O^{2+}$ (oxygen vacancy) $= 2Si^{4+}$ (Pawley et al. 1993; Litasov et al. 2007). The Al substitution can affect the elastic properties of stishovite and post-stishovite transition, which are of great importance in understanding seismic wave properties of subducting MORB in the deep Earth. Specifically, previous X-ray diffraction studies have shown that 0.7-2.1 mol% Al substitution can reduce the density of stishovite by ~0.2-1.2% at 15 GPa (Ono et al. 2002; Lakshtanov et al. 2005; Zhang et al. 2022; Criniti et al. 2023). Previous ultrasonic data have shown that 1.3 mol% Al substitution reduces the shear wave velocity (V_S) and compressional wave velocity (V_P) of stishovite by ~4.1% and ~3.5%,

respectively, at 18.4 GPa and 1700 K (Gréaux et al. 2016). These findings have been used to interpret the negative sound velocity perturbation in the mantle transition zone (Simmons and Gurrola 2000; Tauzin et al. 2013; Gréaux et al. 2016).

Of particular interest in deep-mantle seismology is the role of Al dissolution on the velocity reductions across the post-stishovite transition (Lakshtanov et al. 2005, 2007b; Bolfan-Casanova et al. 2009; Umemoto et al. 2016; Zhang et al. 2022; Criniti et al. 2023). Al-bearing stishovite transforms into a $CaCl_2$-typed post-stishovite phase with the transition pressure ranging from 50-55 GPa in Al-free stishovite to 16-24 GPa in stishovite with approximately 1.3-2.4 mol% Al (Andrault et al. 1998; Lakshtanov et al. 2007b; Bolfan-Casanova et al. 2009; Zhang et al. 2022). That is, Al substitution in stishovite can significantly lower the post-stishovite transition pressure. Although the sound velocity across the Al-dependent transition has not been experimentally measured, the Al effect on the post-stishovite transition mechanism is the key to shed light on the elasticity across the transition (Carpenter et al. 2000; Umemoto et al. 2016; Zhang et al. 2021, 2022; Criniti et al. 2023). Previous works on the high-pressure Raman optic modes and spontaneous strains of stishovite crystals with 1.3, 2.1, and 2.4 mol% Al (denoted as Al1.3-SiO_2, Al2.1-SiO_2, and Al2.4-SiO_2) have shown that the Raman shifts of B_{1g} and A_{1g} modes change linearly with symmetry-breaking strain (e_1-e_2), indicating a pseudo-proper typed ferroelastic transition. This observation is consistent with the transition mechanism in the pure-endmember stishovite (Lakshtanov et al. 2007b; Zhang et al. 2022). Landau modeling on this type of transition further shows a maximum V_S reduction of ~29 % in the Al1.3-SiO_2 and Al2.1-SiO_2 crystals, which has been used to explain small-scale negative V_S anomalies beneath subduction region in the upper part of the lower mantle (Niu et al. 2003; Kaneshima 2016, 2019; Zhang et al. 2022). However, a recent study on the Al1.7-SiO_2 crystal has shown that after the post-stishovite transition at ~16 GPa, the B_{1g} mode continues to soften up to ~20 GPa and then flattens up to ~30 GPa (Criniti et al. 2023). This leads to a non-linear coupling or a decoupling between the soft optic mode and the spontaneous strain, and thus, the transition is not classified as a pseudo-proper type. This discrepancy may be due to the peak identification of the B_{1g} or A_{1g} mode in Raman spectra or the use of twinned crystals in the experiments. Unlike Lakshtanov et al. (2007b) and Zhang et al. (2022), where only one dominant peak was observed in the Raman

shift region of the B_{1g} or A_{1g} mode at high pressure, Criniti et al. (2023) observed 3-4 intense peaks in the region of 180-230 cm^{-1} at 14.8-38.1 GPa such that the optic mode identification became challenging.

High-pressure SCXRD data with refined atomic positions, bond lengths, and bond angles are well documented in pure-endmember stishovite and post-stishovite (Sugiyama et al. 1987; Ross et al. 1990; Yamanaka et al. 2002; Zhang et al. 2023). In pure-endmember stishovite, the oxygen position and bond angles change little (< 1.3%) with increasing pressure up to ~51.4 GPa. Importantly, apical Si-O bond is initially longer than the equatorial Si-O bond, and due to different compressibility, their bond lengths cross over at ~51.4 GPa where a pseudo-proper typed transition occurs (Zhang et al. 2023). Refinement of SCXRD data on Al0.6-SiO_2 and Al1.7-SiO_2 crystals at ambient conditions shows minimal changes in atomic positions and slight alterations in bond lengths and bond angles within data uncertainties (Smyth et al. 1995; Criniti et al. 2023). In the Al1.7-SiO_2 crystal, the Al substitution shifts the transition down to ~16 GPa, but the trend and slope of (Si,Al)-O bond lengths and the crossover pressure are similar to those in pure-endmember SiO_2 (Criniti et al. 2023). Because the crossover of two Si-O bond lengths can be correlated to the vanishing of shear modulus (C_{11}-C_{12}) (Zhang et al. 2021, 2023), the Al1.7-SiO_2 crystal would have a shear softening at ~51 GPa. This conclusion is inconsistent with the shear softening pressure reported in other Al-bearing single crystals in literatures (Lakshtanov et al. 2007b; Zhang et al. 2022). This discrepancy likely results from the severe twinning in the Al1.7-SiO_2 crystal throughout the transition and in the post-stishovite phase, which is indicated from both Raman spectra, where multiple peaks were observed for the B_{1g} or A_{1g} mode as mentioned earlier, and SCXRD data, where multiple lattices with different crystallographic orientations were found (Criniti et al. 2023). Because the peak position of the B_{1g} or A_{1g} mode is sensitive to the Al content (Kingma et al. 1995; Lakshtanov et al. 2007a; Zhang et al. 2022), different Raman peak positions mean that each twin component may have different Al contents, and thus, different compressional behaviors at high pressure. Also, each twin component undergoes deformation due to not only quasi-hydrostatic compression from the pressure medium and but also additional stress from other twin components, potentially affecting the high-pressure SCXRD data (Parsons 2003). To overcome these issues and gain a better

understanding of the transition mechanism and elastic properties, one needs to conduct SCXRD experiments on high-quality Al-bearing stishovite crystals without apparent twinning to obtain high-quality structural refinement results. The combination of high-quality crystallographic information, together with Raman optic mode, spontaneous strains, and elasticity, can help unravel the effects of Al on the transition mechanism and elastic properties across the post-stishovite transition.

In this study, synchrotron SCXRD experiments have been conducted on high-quality Al1.3-SiO_2 and Al2.1-SiO_2 crystals up to 41.4 GPa and 41.1 GPa, respectively, using Boehler-Almax designed anvils in diamond anvil cells (DACs). Refinements of high-pressure SCXRD data show space group, atomistic, and octahedral parameters of these crystals at high pressure. The Al1.3-SiO_2 and Al2.1-SiO_2 crystals underwent stishovite (space group $P4_2/mnm$) to $CaCl_2$-typed post-stishovite (space group *Pnnm*) transition between 20.4-22.5 GPa and 14.3-16.4 GPa, respectively, where O coordinates split, apical and equatorial (Si,Al)-O bond lengths cross over, and (Si,Al)O_6 octahedral distortion vanishes. The Al substitution results in a more rapid reduction in the O coordinate, stiffer apical (Si,Al)-O bond but softer equatorial (Si,Al)-O bond, and a less distorted (Si,Al)O_6 octahedron at high pressure. Together with complimentary optical Raman data, these Al-dependent atomistic and octahedral parameters are used to understand the transition mechanism and elastic properties, including elastic modulus (C_{ij}), adiabatic bulk and shear modulus (K_S and G), and sound velocities (V_S and V_P), across the post-stishovite transition.

Experimental details

Al-bearing stishovite crystals were synthesized using both 5000-ton and 1000-ton Kawai-type multi-anvil apparatus with run # 5K3302 and 1K2965, respectively, at the Institute for Planetary Materials at Okayama University. Details of sample synthesis and characterization can be found in Zhang et al. (2022). Briefly, run # 5K3302 was synthesized at 20 GPa and 1973 K for 16.5 hours while run # 1K2965 was synthesized at 19.2 GPa and 1973 K for 7 hours. Qualitative chemical mappings on selected large crystals using a scanning electron microscopy with energy dispersive X-ray spectroscopy (SEM/EDS) have shown that Si, Al, and O elements distribute

146 homogeneously throughout the crystals. Further quantitative chemical analysis using a JEOL
147 Electron Microprobe (EPMA) have shown that the crystals contain 3.43(6) wt% Al_2O_3 (1.34(2)
148 mol% Al; denoted as Al1.3-SiO_2) in run # 5K3302 and 5.37(4) wt% Al_2O_3 in run # 1K2965
149 (2.10(2) mol% Al; denoted as Al2.1-SiO_2). Water contents were estimated to be 0.25(5) wt%
150 H_2O (0.55(11) mol% H) in Al1.3-SiO_2 and 0.27(5) wt% H_2O (0.59(11) mol% H) in Al2.1-SiO_2
151 using an unpolarized Fourier-transform infrared spectroscopy (FTIR). Analysis of synchrotron
152 SCXRD data at ambient shows a tetragonal structure with the $P4_2/mnm$ space group (No. 136)
153 for these crystals (Table 1).

154

155 Short-symmetric DACs equipped with 300 μm Boehler-Almax designed diamond anvils and
156 tungsten-carbide seats with a large aperture of ~80° (4θ) were used in the high-pressure SCXRD
157 measurements. A piece of 260 μm thick rhenium gasket was pre-indented to ~35 μm thick, and a
158 hole with a diameter of 190 μm was drilled in the center of the pre-indented area to serve as a
159 sample chamber. To obtain sufficient deflection data for reliable refinements of crystal structures
160 at high pressure, we double-side polished two Al1.3-SiO_2 crystals with (3.2, -2.3, -0.9) and (1.9, -
161 3.1, 1.4) orientations and three Al2.1-SiO_2 crystals with (2.7, -0.0, 0.1), (1.6, 3.8, 0.4), and (3.4, -
162 0.6, 1.6) orientations down to 10-15 μm and cut them to approximately 20 by 30 μm big. These
163 two batches of crystals were loaded into the sample chamber of a DAC separately, together with
164 platinum (Pt) and ruby as pressure calibrants. Ruby was used to determine pressure after gas
165 loading while Pt was used to measure pressure during in situ SCXRD measurements. Two Al1.3-
166 SiO_2 crystals or three Al2.1-SiO_2 crystals were placed at an equal distance to Pt to minimize the
167 stress difference across the crystals (Fig. 1). Neon was finally loaded into the chamber up to
168 21,000 Psi as a pressure medium in the Mineral Physics Laboratory at the University of Texas at
169 Austin. The pressure after neon loading was measured by shifts of the fluorescence peak of ruby
170 (Dewaele et al. 2008).

171

172 High-pressure synchrotron SCXRD experiments were performed on the Al1.3-SiO_2 and Al2.1-
173 SiO_2 crystals at the beamline 13ID-D of the GSECARS, Advanced Photon Source, Argonne
174 National Laboratory. An incident X-ray beam with 0.2952 Å wavelength and 10% intensity was
175 focused on 3 by 3 μm areas of each crystal. The sample stage was rotated over ±33° about its

vertical axis. XRD frames were collected 1 or 2 s at every 0.5° of the rotation by a CdTe Pilatus 1 M detector. The total number of frames is 132 for each crystal. A membrane setup was used to control pressure in DAC which was determined by the unit-cell volume of Pt based on its equation of state (EoS) parameters (Fei et al. 2007). The SCXRD data were collected every 2-3 GPa up to 41.4 GPa for Al1.3-SiO_2 and up to 41.1 GPa for Al2.1-SiO_2 crystals. Together with the use of the Boehler-Almax anvils with an opening (4θ) of ~80°, the experimental setup allowed us to obtain more reflection spots especially with small *d*-spacings and to avoid intensity saturations of the spots.

We followed the same procedure as Zhang et al. (2022a) to resolve and refine crystal structures. To begin with, CrysAlisPRO software was used to find a proper unit cell, calculate unit-cell parameters, determine intensity for each *hkl* reflection, and then correct for absorption using the SCALE3 ABSPACK scaling algorithm for each crystal (Rigaku 2015). Subsequently, two datasets of Al1.3-SiO_2 or 3 datasets of Al2.1-SiO_2 crystals were then combined at each given pressure as an input for the structural analysis using JANA software (Petrícek et al. 2014). The space group and crystal structure of the samples were determined using a charge-flipping algorithm (Petrícek et al. 2014). Site occupancies of Si and Al were fixed to be 0.960 Si and 0.040 Al for the Al1.3-SiO_2 crystal and 0.937 Si and 0.063 Al for the Al2.1-SiO_2 crystal based on the EPMA analysis results (Zhang et al. 2022). The H atom was not included in the structural refinement due to its low concentration and small atomic scattering factor (i.e., low diffracting power). Eventually, the atomic coordinates and isotropic/anisotropic displacement parameters were refined, and the quality of the refinements were evaluated by three residual *R*-factors (R_{int}, R_1, and R_2; Table 1). Refined structural parameters, including bond lengths, bond angles, and polyhedral parameters, were measured and calculated using VESTA software (Momma and Izumi 2011). The Crystallographic Information Framework (CIF) files for both Al1.3-SiO_2 and Al2.1-SiO_2 crystals at different pressures can be found in supplementary materials.

Results

Structural refinement

Analysis of raw SCXRD patterns show a range of 66-439 total reflections for the Al1.3-SiO_2 crystal and 106-423 total reflections for the Al2.1-SiO_2 crystal at high pressure (Figs. 1a and 1b). These reflection spots exhibit a circular shape and their full-width at half maximum (FWHM) remains unchanged between 0.04-0.09° under pressures up to ~41 GPa in both Al1.3-SiO_2 and Al2.1-SiO_2 crystals (Fig. 1c), indicating that the remarkable single-crystal quality remains unaltered throughout the compression (Zhang et al. 2023). The original reflections were subsequently categorized into 31-66 and 40-64 unique reflections for the Al1.3-SiO_2 and Al2.1-SiO_2 crystal, respectively, which were used to calculate lattice parameters under high pressure (Table 1). The R_{int} values were obtained to be in a range of 1.3-13.8 %, indicating a good quality of our derived lattice parameters (Table 1). Analysis of lattice parameters at high pressure shows that *a* axis splits into *a* and *b* axis at ~16.1 GPa in Al1.3-SiO_2 and ~21.1 GPa in Al2.1-SiO_2, while the length of *c* axis and unit-cell volume decrease continuously throughout the compression (Fig. S1). Based on the Birch-Murnaghan EoS fitting of the data, the ambient isothermal bulk modulus (K_{T0}) and its first-order pressure derivative (K_{T0}') for Al-bearing stishovite were derived to be K_{T0} = 301(2) GPa and K_{T0}' = 4 (fixed) for Al1.3-SiO_2 and K_{T0} = 292(2) GPa and K_{T0}' = 4 (fixed) for Al2.1-SiO_2 (Table S1) (Angel 2000). These results are consistent with the published high-pressure lattice parameters and EoS parameters for the Al-bearing stishovite (Zhang et al. 2022).

To further determine the crystal's space group, a subset of 27-45 and 31-70 reflections, where the intensity (I) exceeds three times the standard deviation (σ) of the intensity (i.e., $I > 3\sigma(I)$), were selected for the Al1.3-SiO_2 and Al2.1-SiO_2 crystals, respectively. The Al1.3-SiO_2 and Al2.1-SiO_2 crystals maintain a tetragonal structure with the $P4_2/mnm$ space group (No. 136) up to 20.4 and 14.3 GPa, whereas they adopt an orthorhombic structure with the *Pnnm* space group (No. 58) above 22.5 and 16.4 GPa, respectively (Fig. 2). Thus, the stishovite-to-post-stishovite transition occurs at 20.4-22.5 GPa in the Al1.3-SiO_2 crystal and at 14.3-16.4 GPa in the Al2.1-SiO_2 crystal, consistent with previous transition pressures determined by Raman and XRD analyses on the same crystals (Zhang et al. 2022). The refined symmetries of both stishovite and post-stishovite phases mean that the Si or Al atoms are located at (0, 0, 0) and the O atoms are located at (O*x*, O*y*, 0). The coordinates O*x* and O*y*, together with isotropic/anisotropic displacement parameters

of all atoms, were further refined until the R_1 and R_2 values reached the minimal. The final R_1 and R_2 values are in a range of 4.8-11.6 % and 5.6-14.7 %, respectively, indicating a good quality of our refined structural models (Table 1).

Atomistic parameters

Analysis of refined oxygen coordinates shows that O*x*(*y*) in the stishovite structure decreases monotonically from 0.3067(3) at ambient pressure to 0.3021(9) at 20.4 GPa for Al1.3-SiO_2 and from 0.3066(5) at ambient pressure to 0.3026(7) at 14.3 GPa for Al2.1-SiO_2 (Figs. 3a and 3d). Across into the post-stishovite phase, the oxygen coordinate splits into O*x* and O*y*, indicating a symmetry breaking from tetragonal to orthorhombic structure (Andrault et al. 1998). O*y* increases to 0.3143(10) and O*x* decreases to 0.2813(9) at 41.4 GPa in the Al1.3-SiO_2 crystal, while O*y* increases to ~0.313 at ~27 GPa and becomes unchanged up to 41.1 GPa and O*x* decreases to 0.2803(17) at 41.1 GPa in the Al2.1-SiO_2 crystal.

The obtained atomic positions, together with lattice parameters, can be used to calculate bond lengths and bond angles based on the symmetry and geometry of the crystal structure at given pressure. As the Al1.3-SiO_2 crystal is compressed from ambient pressure to 41.4 GPa, the mean bond length of apical (Si,Al)-O3 bonds decreases significantly from 1.820(1) Å to 1.699(4) Å while that of equatorial (Si,Al)-O1(2) bonds deceases gently from 1.761(1) to 1.736(3), resulting in a crossover of two bond lengths at ~21 GPa (Figs. 3b and 3e). Similarly, the significant decrease of apical (Si,Al)-O3 bond length and gentle decrease of equatorial (Si,Al)-O1(2) bond lead to a crossover of two bond lengths at ~17 GPa in the Al2.1-SiO_2 crystal. On the other hand, the mean bond angle of ∠(Si,Al)-O3-(Si,Al) in the stishovite phase increases as the pressure increases, going from 130.65(4)° at ambient pressure to 130.99(10)° at 20.4 GPa for Al1.3-SiO_2 and from 130.70(6)° at ambient pressure to 130.96(8)° at 14.3 GPa for Al2.1-SiO_2 (Figs. 3c and 3f). After the post-stishovite transition, this angle exhibits a gradual increase, reaching 131.04(11)° at 41.4 GPa for Al1.3-SiO_2 and 131.26(15)° at 41.4 GPa for Al2.1-SiO_2. However, ∠O1-(Si,Al)-O1 behaves inversely under pressure, decreasing from 98.71(7)° at ambient pressure to 98.02(19)° at 20.4 GPa for Al1.3-SiO_2 and from 98.60(11)° at ambient pressure to

98.08(15) at 14.3 GPa for Al2.1-SiO_2. In the post-stishovite phase, this decrease accelerates, reaching 96.98(19)° at 41.4 GPa for Al1.3-SiO_2 and 96.60(40)° at 41.1 GPa for Al2.1-SiO_2. Finally, ∠O1-(Si,Al)-O3 is constrained to be 90° by the symmetry of tetragonal stishovite, while it changes little (<0.5°) up to ~41 GPa in the post-stishovite phase for both Al1.3-SiO_2 and Al2.1-SiO_2.

(Si,Al)O_6 octahedron

The refined atomic positions can also be used to determine the behavior of the (Si,Al)O_6 octahedron, a basic structural unit in the Al-bearing stishovite and post-stishovite structures (Fig. 4). The mean volume of the (Si,Al)O_6 octahedron (V_{oct}) decreases continuously from 7.439(7) Å^3 at ambient conditions to 6.775(22) Å^3 at 41.4 GPa for Al1.3-SiO_2 and 7.471(12) Å^3 at ambient conditions to 6.833(35) Å^3 at 41.1 GPa for Al2.1-SiO_2 (Figs. 4a and 4d). This observation, together with a continuous volume change across the transition (Fig. S1), indicates a second-order characteristic of the Al-bearing post-stishovite transition (Carpenter et al. 2000).

The deformation of the (Si,Al)O_6 octahedron can be evaluated by distortion index (D) and bond angle variance (σ^2), which describe the deviation from an ideal octahedral geometry with respect to its bond length and bond angle, respectively. D can be calculated by a formula of $D(\%) = \frac{100}{6}\sum_{i=1}^{6}|l_i - l_{avg}|/l_{avg}$, where l_i is the i^{th} mean (Si,Al)-O bond length in an octahedron and l_{avg} is the average of six mean (Si,Al)-O bond length in an octahedron (Renner and Lehmann 1986). The D value of both Al1.3-SiO_2 and Al2.1-SiO_2 crystals decreases from ~1.5% at ambient conditions to zero at transition pressure (Figs. 4b and 4e), indicating that the (Si,Al)O_6 octahedron becomes less distorted under compression in the stishovite phase. Across into the post-stishovite phase, D increases monotonously with increasing pressure up to 0.956(3)% at 41.4 GPa for Al1.3-SiO_2 and 1.291(7)% at 41.1 GPa for Al2.1-SiO_2, indicating that the (Si,Al)O_6 octahedron becomes more distorted under compression in the post-stishovite phase. On the other hand, σ^2 can be calculated by $\sigma^2(deg^2) = \frac{1}{11}\sum_{i=1}^{12}(\alpha_i - 90°)^2$, where α_i is the i^{th} mean ∠O-(Si,Al)-O in an octahedron (Robinson et al. 1971). The σ^2 value decreases from 27.56(3) deg^2 at

ambient pressure to 23.36(7) deg^2 at 20.4 GPa for Al1.3-SiO_2 and from 26.92(4) deg^2 at ambient pressure to 23.72(5) deg^2 at 14.3 GPa for Al2.1-SiO_2. Across into the post-stishovite phase, σ^2 decreases faster down to 17.72(6) deg^2 at 41.4 GPa for Al1.3-SiO_2 and to 15.76(8) deg^2 at 41.1 GPa for Al2.1-SiO_2. This means that the angle distortion in the (Si,Al)O_6 octahedron diminishes under pressure and this diminishing becomes faster in the post-stishovite phase.

As the tetragonal symmetry starts to breaks down into the orthorhombic structure, the (Si,Al)O_6 octahedron rotates about the *c* axis in the post-stishovite phase (Fig. S2). The mean rotation angle, Φ, can be calculated by $\Phi(°) = 45° - \arctan(a \cdot 0x/b/0y)$ (Range et al. 1987; Zhang et al. 2023). The Φ value increases significantly up to ~2.5° at ~30 GPa and ~23 GPa for the Al1.3-SiO_2 and Al2.1-SiO_2 crystal, respectively, and then gradually increases up to ~4° at ~41 GPa for both crystals (Fig. S2). This nonlinear increase under pressure results from a nonlinear pressure dependence of the Raman shift of the A_g mode which represents a rotational vibration of O in the (Si,Al)O_6 octahedron about the *c* axis (Hemley et al. 1986).

Discussion

To better understand the Al substitution effects on the post-stishovite transition, we compare atomistic and octahedral parameters of Al-bearing stishovite with those of pure-endmember stishovite by Zhang et al. (2023). In this section, we first fit high-pressure atomistic and octahedral data using an EoS or a linear function. This allows us to obtain compressibility or pressure-dependent behavior of these parameters. Subsequently, we discuss the influence of Al substitution on both atomistic and octahedral parameters as well as their high-pressure behaviors. Finally, we compare our results to previous crystallographic data on Al-bearing stishovite to gain further insights on the post-stishovite transition mechanism.

Equations of state and axial incompressibility fitting

Our high-pressure crystallographic data are further evaluated using the Birch-Murnaghan EoS for V_{oct}, an axial EoS for mean (Si,Al)-O bond lengths, and a linear function for atomistic and

octahedral parameters (Tables 4 and S2). First, the third-order Birch-Murnaghan EoS can be expressed as

$$P = (1 + 2f_{oct})^{2.5}\left[3K_{0,oct}f_{oct} + 4.5K_{0,oct}\left(K'_{0,oct} - 4\right)f_{oct}^2\right] \quad (1)$$

where f_{oct} is the Eulerian finite strain, $f_{oct} = \left[\left(V_{0,oct}/V_{oct}\right)^{2/3} - 1\right]/2$; $V_{0,oct}$, $K_{0,oct}$, and $K'_{0,oct}$ are the volume, bulk modulus, and its first-order pressure derivative of the (Si,Al)O_6 octahedron (Birch 1947; Angel 2000). The obtained EoS parameters of Al-bearing stishovite are $K_{0,oct}$ = 351(2) GPa and $K'_{0,oct}$ = 4 (fixed) for the Al1.3-SiO_2 crystal and $K_{0,oct}$ = 357(2) GPa and $K'_{0,oct}$ = 4 (fixed) for the Al2.1-SiO_2 crystal (Table 4). Additionally, an axial third-order EoS is used to fit the mean (Si,Al)-O bond length data (l) at high pressure,

$$P = (1 - 2f_l)^{2.5}\left[-K_{0,l}f_l + 0.5K_{0,l}\left(K'_{0,l} - 4\right)f_l^2\right] \quad (2)$$

where f_l is the axial finite strain, $f_l = [1 - (l_0/l)^2]/2$; l_0, $K_{0,l}$, and $K'_{0,l}$ are the bond length, linear modulus, and its first-order pressure derivative at ambient conditions (Birch 1947; Angel 2000). The fitting yields $K_{0,(Si,Al)-O3}$ = 404(9) GPa and $K_{0,(Si,Al)-O1(2)}$ = 2561(52) GPa for the Al1.3-SiO_2 crystal and $K_{0,(Si,Al)-O3}$ = 368(18) GPa and $K_{0,(Si,Al)-O1(2)}$ = 4007(165) GPa for the Al2.1-SiO_2 crystal, when their $K'_{0,l}$ are fixed as 12 (Table 4). Finally, some atomistic and octahedral parameters of Al-bearing stishovite phase are fitted using a linear function in a form of $M = a_0 + a_1 * P$, where M is the oxygen coordinate, bond angle, distortion index, or bond angle variance; a_0 and a_1 are fitted coefficients which are listed in Table S2.

Al substitution effects on atomistic parameters

Comparison between our results and previous data on pure stishovite shows that 2.1 mol % Al substitution in stishovite leads to Ox(y), ∠(Si,Al)-O3-(Si,Al), and ∠O1-(Si,Al)-O1 change of only ~0.04%, ~0.06%, and ~-0.13%, respectively, at ambient conditions (Smyth et al. 1995; Criniti et al. 2023; Zhang et al. 2023). This indicates that the influence of Al substitution on the oxygen coordinate and bond angle are rather insignificant (Fig. 5a). Moreover, the 2.1 mol% Al substitution increases apical (Si,Al)-O3 bond length by ~0.8% and equatorial (Si,Al)-O1(2) bond length by ~0.5% (Fig. 5b), leading to a larger Al-bearing octahedron and thus a larger unit cell in Al-bearing stishovite compared to that in pure-endmember stishovite (Fig. S1). On the other

hand, the Al effects on the slope of these parameters under pressure are more prominent. Ox(y) and ∠O1-(Si,Al)-O1 decrease faster whereas ∠(Si,Al)-O3-(Si,Al) increases faster under pressure in Al-bearing stishovite than pure-endmember stishovite (Figs. 5d and 5f). Importantly, the equatorial (Si,Al)-O1(2) bond becomes stiffer whereas the apical (Si,Al)-O3 bond becomes softer with the Al substitution (Fig. 5e). Specifically, $K_{0,(Si,Al)-O1(2)}$ is 2.69 times larger whereas $K_{0,(Si,Al)-O3}$ is 1.69 times smaller in the Al2.1-SiO_2 crystal than in pure-endmember stishovite (Zhang et al. 2023). This leads to the crossover of two bond lengths at lower pressure in Al-bearing stishovite.

Al effects on SiO_6 octahedral geometry

The Al-dependent bond lengths and bond angles can result in Al-dependent octahedral parameters (Fig. 6). The (Si,Al)O_6 octahedron volume, V_{oct}, increases with Al substitution mainly due to increased epical and equatorial (Si,Al)-O bond lengths in Al-bearing stishovite (Fig. 6a). The bulk modulus, $K_{0,oct}$, decreases by only ~2 % with 2.1 mol% Al substitution, meaning that the Al substitution slightly increases the compressibility of the (Si,Al)O_6 octahedron at high pressure (Fig. 6d). Moreover, the distortion index, D, of the Al1.3-SiO_2 and Al2.1-SiO_2 crystals is ~15-16 % larger than that of pure-endmember stishovite at ambient conditions, indicating that an Al-bearing (Si,Al)O_6 octahedron is more distorted than a pure SiO_6 octahedron (Fig. 6b). At high pressure, D decreases faster with the Al substitution because of the stiffer (Si,Al)-O1(2) bond and the softer apical (Si,Al)-O3 bond, leading to vanishing of bond length distortion in the (Si,Al)O_6 octahedron at lower pressure (Fig. 6e). Additionally, the angle variance, σ^2, of the Al1.3-SiO_2 and Al2.1-SiO_2 crystals decreases slightly with the Al substitution at ambient conditions (Fig. 6c). It decreases under pressure in Al-bearing stishovite while remains unchanged in pure-endmember stishovite (Fig. 6f). This indicates that the Al substitution leads to bond angles more regular in the Al-bearing (Si,Al)O_6 octahedron.

Comparison to previous studies

The atomistic and octahedral parameters of the Al1.3-SiO_2 and Al2.1-SiO_2 crystals at ambient conditions are compared with those in the literature (Figs. 4 and 5) (Smyth et al. 1995; Criniti et al. 2023; Zhang et al. 2023). However, our refined high-pressure data are not consistent with that of the Al1.7-SiO_2 crystal in Criniti et al. (2023). Unlike our refined structural data which show apparent Al effects at high pressure, the trends and slopes of atomistic and octahedral parameters of their Al1.7-SiO_2 crystal under pressure are similar to those of pure-endmember stishovite, except for $K_{0,oct}$ and the splitting of the O coordinates. $K_{0,oct}$ of the Al1.7-SiO_2 crystal is ~11% lower while the splitting of the O coordinates is smaller than that of our crystals, although the Al1.7-SiO_2 crystal has Al content between our two crystals. This discrepancy could be due to different Al contents in different twinning components that can affect the compressional behavior of the crystal.

Implications

Atomistic understanding of Al substitutional effects on the elasticity of stishovite

Our SCXRD studies reveal Al effects on the atomistic and octahedral parameters which can help understand Al effects on density, bulk modulus, shear modulus, and sound velocities of stishovite. Previous studies have shown that the Al substitution can reduce the density of stishovite at the rate of ~-0.02 g·cm^{-3}/mol% at ambient conditions (Smyth et al. 1995; Ono et al. 2002; Lakshtanov et al. 2007a; Litasov et al. 2007; Zhang et al. 2021, 2022; Criniti et al. 2023). This can be explained by increased apical and equatorial (Si,Al)-O bond lengths and increased V_{oct} in Al-bearing stishovite. Moreover, the 1.7% Al substitution can reduce the bulk and shear modulus by 6.3 or 12.6% and 3.2 or 14.9%, respectively, based on previous Brillouin or ultrasonic studies (Lakshtanov et al. 2007a; Gréaux et al. 2016). The reduction in bulk modulus could be caused by the decrease in both linear modulus of (Si,Al)-O3 bond length and O coordinates with the Al substitution. The reduction in shear modulus could be attributed to a more rapid decrease of the (Si,Al)-O bond length difference under pressure as a result from a stiffer equatorial (Si,Al)-O1(2) and a softer apical (Si,Al)-O3 bond. Specifically, the bond length difference can be correlated with shear modulus along [110] direction, (C_{11}-C_{12})/2, in the stishovite structure (Zhang et al. 2023). That is, (C_{11}-C_{12})/2 decreases as the bond length difference decreases. The more rapid decrease of the (Si,Al)-O bond length difference can thus

result in a reduced shear modulus at given pressure in Al-bearing stishovite. Finally, combined Al effects on density and bulk/shear modulus can lead to a reduction of sound velocity in Al-bearing stishovite.

Al effects on the post-stishovite transition mechanism

The transition mechanism of Al-bearing stishovite can be deduced from an integration of our SCXRD refinement results and recent Raman and spontaneous strain results on the same crystals (Zhang et al. 2022). The SCXRD results have revealed that the Al1.3-SiO_2 and Al2.1-SiO_2 crystals have more compressible apical (Si,Al)-O3 and less compressible equatorial (Si,Al)-O1(2) bond than pure-endmember stishovite, and thus, the crossover of two bonds and the vanishing of the (Si,Al)O_6 distortion occur at much lower pressure (Fig. 7a). This transition pressure coincides well with the tetragonal to orthorhombic transition where the *a* axis splits into *a* and *b* axis, the O coordinate splits, and the (Si,Al)O_6 octahedron starts to rotate about the *c* axis. These crystallographic changes in Al-bearing stishovite across the transition are consistent with that in the pseudo-proper typed transition in pure-endmember stishovite under pressure (Zhang et al. 2023), although the transition pressure is much lower in Al-bearing stishovite. On the other hand, a recent Raman and spontaneous strain study on the same crystals has revealed that the soft B_{1g} mode, as the driving force of the transition, is coupled linearly with the symmetry-breaking strain (e_1-e_2), consistent with the mechanism of a pseudo-proper typed transition (Carpenter et al. 2000; Zhang et al. 2022). These integrated datasets here validate that the Al1.3-SiO_2 and Al2.1-SiO_2 stishovite undergoes a pseudo-proper typed ferroelastic transition frat ~21 GPa and ~17 GPa, respectively.

Our crystallographic data can be used with a pseudo-proper typed Landau model (Carpenter et al. 2000) to provide new insights into Al effects on the driving force of the transition. The free energy difference between post-stishovite and stishovite is a polynomial expression of the order parameter, Q, which describes the driving force of the transition (Carpenter et al. 2000). A previous SCXRD study on pure-endmember stishovite has revealed that Q increases linearly with octahedral rotation angle, Φ, in the pseudo-proper typed post-stishovite transition (Zhang et

al. 2023). A linear fit to the Q-Φ data of our Al1.3-SiO_2 and Al2.1-SiO_2 crystals shows that the Al substitution can increase the slope of the relation (Fig. 7b). That is, at a given Φ, Q is larger, and thus, the free energy difference between post-stishovite and post-stishovite becomes larger in our Al-bearing crystals. Therefore, the Al substitution can stabilize the post-stishovite phase at a relatively lower pressure than the pure-endmember counterpart.

Deep-mantle elasticity

Our crystallographic data can be further correlated with elastic properties to shed light on the Al effects on the elasticity across the post-stishovite transition in the lower mantle. Here, we co-plot C_{ij}, K_S, G, V_P, and V_S as a function of bond length difference between apical (Si,Al)-O3 and equatorial (Si,Al)-O1(2) bonds ($\Delta l_{Si(Al)\text{-}O}$) that reflects the degree of octahedral distortion (distortion index D) (Fig. 8). The C_{ij}, K_S, G, V_P, and V_S values of the Al1.3-SiO_2 and Al2.1-SiO_2 crystals at high pressures were previously derived from Raman and EoS data within the framework of Landau theory (Carpenter et al. 2000; Zhang et al. 2022). All C_{ij}'s of Al-bearing stishovite increase with decreasing $\Delta l_{Si(Al)\text{-}O}$, except for C_{11} which slightly decreases until $\Delta l_{Si(Al)\text{-}O}$ vanishes (Figs. 8a and 8b). Compared to the pure-endmember stishovite, the Al effect on C_{ij}'s at an initial $\Delta l_{Si(Al)\text{-}O}$ value of ~0.05 Å is insignificant, except for shear moduli C_{44} and C_{66} which are ~6-8 % lower in Al1.3-SiO_2 and Al2.1-SiO_2. This reduction in shear moduli at ~0.05 Å $\Delta l_{Si(Al)\text{-}O}$ may result from the decreased oxygen coordinate $Ox(y)$ and octahedral angle variance σ^2 in Al-bearing stishovite that can make the shear deformation along the principle planes (i.e., the (100), (010), (001) planes) easier. As $\Delta l_{Si(Al)\text{-}O}$ decreases, the slopes of C_{ij}'s of Al-bearing stishovite are more gentle than that of pure-endmember stishovite, indicating that the Al substitution can diminish the influence of $\Delta l_{Si(Al)\text{-}O}$ and D on C_{ij}'s. In other words, at a given bond length difference and octahedral distortion, the Al substitution can lead to lower C_{ij}'s. Across into the post-stishovite phase, as $\Delta l_{Si(Al)\text{-}O}$ becomes negative, elastic moduli C_{11}, C_{13}, and C_{44} split into pairs of (C_{11} and C_{22}), (C_{13} and C_{23}), and (C_{44} and C_{55}). This splitting in Al1.3-SiO_2 and Al2.1-SiO_2 are smaller than that in pure-endmember SiO_2, indicating again that the Al substitution can lead to a smaller change in C_{ij}'s at a certain degree of octahedral distortion. Furthermore, the Al effect on K_S, G, V_P, and V_S are similar to that on C_{ij}'s (Figs. 8c and 8d). That is, at given $\Delta l_{Si(Al)\text{-}O}$ and D, the K_S, G, V_P, and V_S values of Al1.3-SiO_2 and Al2.1-SiO_2 are ~2-31 %, ~8-36 %, ~2-

11 %, and ~4-12 % lower than that of pure-endmember SiO_2, respectively. Particularly, when the bond length distortion vanishes (i.e., $\Delta l_{Si(Al)-O} = 0$), the Al substitution enhances maximum G, V_P, and V_S reduction during the transition.

Our SCXRD data have revealed the role of the Al substitution in the elastic properties and transition mechanism across the post-stishovite transition, and thus, can provide new insights into geophysical behavior of subducted mid-ocean ridge basalt (MORB) within the mantle transition zone and the lower mantle. The decrease in K_S and G with the Al substitution in stishovite could be due to smaller O coordinates, softer (Si,Al)-O3 bonds, and less distorted $(Si,Al)O_6$ octahedra. At a given degree of the $(Si,Al)O_6$ octahedra distortion, the Al substitution leads to smaller K_S, G, V_P, and V_S values in stishovite phase. This reduction in sound velocities can be used to explain -3.4% V_P and -4.2% V_S perturbations in the mantle transition zone (Simmons and Gurrola 2000; Tauzin et al. 2013; Gréaux et al. 2016). On the other hand, our SCXRD data, together with previous Raman optic modes and spontaneous strains (Zhang et al. 2022), have shown that the Al substitution would not change the transition mechanism in stishovite, but significantly reduces transition pressure through a faster decrease of the (Si,Al)-O bond length difference under pressure. At $\Delta l_{Si(Al)-O} = 0$ where the post-stishovite transition occurs, G, V_P, and V_S reduce with the Al substitution. This Al-dependent transition pressure and elasticity can be used to explain the seismically-observed small-scale V_S anomalies beneath subduction regions in the shallow lower mantle (Niu et al. 2003; Lakshtanov et al. 2007b; Kaneshima 2016, 2019; Zhang et al. 2022).

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