Elasticity of Hydrated Al-Bearing Stishovite and Post-Stishovite: Implications for Understanding Regional Seismic $V_S$ Anomalies Along Subducting Slabs in the Lower Mantle

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Abstract Seismic studies have found seismic scatterers with $-2$ to $-12\%$ shear velocity anomalies along some subducting slabs at 700–1900 km depth. The ferroelastic post-stishovite transition in subducted mid-ocean ridge basalt (MORB) has been linked to these seismic features, but compressional and shear wave velocities ($V_P$ and $V_S$) and full elastic moduli ($C_{ij}$) of Al,H-bearing stishovite and post-stishovite at high pressure remain uncertain. Here we have determined Raman shifts of optic modes and equation of state parameters of two hydrated Al-bearing stishovite crystals, Al1.3-SiO$_2$ (1.34 mol% Al and 0.55 mol% H) and Al2.1-SiO$_2$ (2.10 mol% Al and 0.59 mol% H), up to ~70 GPa in diamond anvil cells coupled with Raman spectroscopy and X-ray diffraction. The experimental data are modeled using a pseudoproper Landau theory to derive full $C_{ij}$ and sound velocities across the post-stishovite transition at high pressure. The Al and H dissolution in stishovite significantly reduces the transition pressure to 21.1 GPa in Al1.3-SiO$_2$ and to 16.1 GPa in Al2.1-SiO$_2$, where the transition is manifested by approximately 29% $V_S$ reduction. Considering that stishovite with approximately 1.3 mol% Al and 0.6 mol% H could account for 20 vol% in subducted MORB at the top-lower mantle, the Al,H-bearing post-stishovite transition with a Clapeyron slope of 65 K/GPa would occur at about 1060 km depth with $-7(4)\%$ $V_S$ anomaly. The $V_S$ anomalies across the Al,H-bearing post-stishovite transition can help explain the seismically-observed depth-dependent $V_S$ anomalies along some subducting slabs in the top- to mid-lower-mantle depths including the Tonga subducting slab.

Plain Language Summary Seismologists have found that shear wave travels 2%–12% slower along some regions of subducting slabs at 700–1,900 km depths than the surrounding lower mantle. This observation cannot be explained by the presence of cold subducting oceanic crusts alone, but the transition from stishovite to post-stishovite could be a possible cause. Stishovite is a high-pressure dense silica polymorph that makes up about one fifth volume of subducting mid-ocean ridge basalt in the lower mantle. We designed high-pressure Raman spectroscopy and X-ray diffraction experiments to probe lattice vibration modes and lattice parameters, respectively, of Al,H-bearing stishovite and post-stishovite. These results are used to evaluate the speed of sound across the post-stishovite transition. Our study shows that the shear wave velocity of stishovite with 1.3–2.1 mol% Al and 0.5–0.6 mol% H significantly slows down by ~29% at 16–21 GPa. If one fifth volume of the subducting oceanic crust is made of stishovite with 1.3 mol% Al and 0.6 mol% H, the velocity reduction across the transition could be ~7% at ~1,060 km depth. Regional seismic observations of $V_S$ anomalies along some subducting slabs in the top- to mid-lower mantle can be explained by the presence of the Al,H-bearing post-stishovite transition.

1. Introduction

Seismic tomographic studies have revealed wide-spread stagnant slabs in the mantle beneath subduction zones (Fukao & Obayashi, 2013). The subducting slabs contain Mid-Ocean Ridge Basalt (MORB) and other crustal and sedimentary materials that are chemically and physically distinct from the lithospheric mantle (Ringwood, 1975). As slab subduction occurs deeper into the lower mantle, basaltic materials are expected to exhibit distinct mineralogy and physical properties that may be revealed seismically (Ishii et al., 2019; Rost et al., 2008). Compared with the mantle lithosphere of approximately 100–200 km thick, the oceanic crust is only ~7 km thick...
so interpretations of seismic images for the subducting MORB materials in the lower mantle have been challenging. Specifically, global seismic tomography has a length resolution of hundreds of kilometers that could not be used to detect the subducted basalt (or eclogite) in the mantle (Fukao & Obayashi, 2013). On the other hand, analyses of short period seismic-wave scattering can provide a much better spatial resolution in the order of ~10 km in the mantle (Rost et al., 2008). Insofar, these short period seismic studies have revealed the occurrence of many regional seismic scatterers with a number of distinct features: (a) slower shear wave velocity ($V_S$) anomaly up to ~12% reduction, no significant compressional wave velocity ($V_P$) anomaly, and sometimes higher density ($\rho$) anomaly at 700–1,900 km depth (Niu, 2014; Niu et al., 2003); (b) planar geometry with several to tens of kilometers in thickness and tens to hundreds of kilometers in length; (c) occurrence within or beneath the subduction slab along the circum-Pacific region, but the frequency of observations decreases from top- to mid-lower mantle (Haugland et al., 2017; Kaneshima, 2019; Li & Yuen, 2014; Vinnik et al., 2001). These features are thought to be indicative of the presence of ancient subducted basalts in the lower mantle (Kaneshima & Helffrich, 1999).

To decipher the aforementioned seismic observations at depths, sound velocities and densities of major constituent minerals at relevant pressure-temperature ($P$-$T$) conditions of the subducted slabs are critically needed. Subducted MORB materials at the upper part of the lower mantle are expected to contain approximately 20 vol% stishovite, 30 vol% CaFe$_2$O$_4$-type phase (CF) or new hexagonal phase (NAL), 30 vol% bridmanite (Bgm), and 20 vol% Ca-perovskite (CaPv; Ishii et al., 2019). Previous studies have shown that sound velocities of these phases except stishovite fall between those of bridmanite and ferropericlase, the two most abundant minerals in a pyrolyte compositional model in the lower mantle (Gréaux et al., 2019; Wu et al., 2016; Xu et al., 2008; Yang et al., 2015). That is, their velocity characteristics could not be used to reconcile the observations of small-scale seismic $V_S$ anomalies along subducing slabs in the lower mantle. However, their occurrence could contribute to seismic observations of enhanced densities in some regions (Hirose et al., 2005; Niu, 2014; Niu et al., 2003; Sun et al., 2016). On the other hand, the rutile-type stishovite displays much higher sound velocities than typical mantle minerals (Yang & Wu, 2014; Zhang et al., 2021), although its density is similar to that of mineral aggregates in a pyrolyte composition (Fischer et al., 2018; Irfune et al., 2010). Stishovite undergoes a pseudoproper ferroelastic transition to a CaCl$_2$-type post-stishovite phase with a spontaneous strain (Carpenter et al., 2000; Hemley et al., 2000). For pure-endmember stishovite (SiO$_2$), the distortion transition occurs at 55 GPa and 300 K and is associated with a drastic $V_S$ reduction of ~26% and a mild $V_P$ reduction of ~10%, but the density continuously increases with increasing pressure (Zhang et al., 2021). It has been theoretically shown that subducted MORB with 20 vol% stishovite undergoing the post-stishovite transition could produce a $V_S$ reduction of up to ~6.5% and a $V_P$ reduction of up to ~1.5% at the mid-lower-mantle depth that can help explain seismic wave velocities (Wang et al., 2020). However, the post-stishovite transition has a positive Clapeyron slope of 65 K/GPa and would occur at ~1,800 km depth at relevant $P$-$T$ conditions of a cold subducting slab (77 GPa and 1706 K; Fischer et al., 2018). The transition depth is thus too deep to be consistent with these aforementioned regional seismic $V_S$ anomalies at shallower lower mantle depths.

Based on previous geochemical and petrological studies (Gale et al., 2013), subducted MORB materials can contain ~10–19 wt% alumina (or ~4.3–8.1 mol%) which can partition into stishovite crystals. Multi-anvil apparatus experiments on element partitioning in a basaltic system have revealed that the Al content in stishovite crystals can vary from ~0.03–0.67 mol% at 20–26 GPa and 1,473–2,073 K conditions (Litasov et al., 2007; Lakshtanov et al., 2020). Experiments, Fourier-transform infrared spectroscopy (FTIR) analyses showed that Al-bearing stishovite crystals contain approximately 0.03–0.67 mol% H at 20–26 GPa and 1,473–2,073 K conditions (Litasov et al., 2007). That is, their velocity characteristics could not be used to reconcile the observations of small-scale seismic $V_S$ anomalies along subducing slabs in the lower mantle. However, their occurrence could contribute to seismic observations of enhanced densities in some regions (Hirose et al., 2005; Niu, 2014; Niu et al., 2003; Sun et al., 2016). On the other hand, the rutile-type stishovite displays much higher sound velocities than typical mantle minerals (Yang & Wu, 2014; Zhang et al., 2021), although its density is similar to that of mineral aggregates in a pyrolyte composition (Fischer et al., 2018; Irfune et al., 2010). Stishovite undergoes a pseudoproper ferroelastic transition to a CaCl$_2$-type post-stishovite phase with a spontaneous strain (Carpenter et al., 2000; Hemley et al., 2000). For pure-endmember stishovite (SiO$_2$), the distortion transition occurs at 55 GPa and 300 K and is associated with a drastic $V_S$ reduction of ~26% and a mild $V_P$ reduction of ~10%, but the density continuously increases with increasing pressure (Zhang et al., 2021). It has been theoretically shown that subducted MORB with 20 vol% stishovite undergoing the post-stishovite transition could produce a $V_S$ reduction of up to ~6.5% and a $V_P$ reduction of up to ~1.5% at the mid-lower-mantle depth that can help explain seismic wave velocities (Wang et al., 2020). However, the post-stishovite transition has a positive Clapeyron slope of 65 K/GPa and would occur at ~1,800 km depth at relevant $P$-$T$ conditions of a cold subducting slab (77 GPa and 1706 K; Fischer et al., 2018). The transition depth is thus too deep to be consistent with these aforementioned regional seismic $V_S$ anomalies at shallower lower mantle depths.

Based on previous geochemical and petrological studies (Gale et al., 2013), subducted MORB materials can contain ~10–19 wt% alumina (or ~4.3–8.1 mol%) which can partition into stishovite crystals. Multi-anvil apparatus experiments on element partitioning in a basaltic system have revealed that the Al content in stishovite increases from ~0.5 mol% at 22 GPa to ~1.5 mol% at 33 GPa (Ishii et al., 2019; Ono et al., 2001). Additionally, chemical analysis of mineral inclusions in natural diamonds from the subducted eclogitic assemblage also shows the presence of nearly Al-free silica (~0.06 mol% Al) in association with Al$_2$SiO$_5$ phase (Zedgenizov et al., 2015). This indicates the possible presence of Al-bearing stishovite at lower-mantle depths, although naturally occurring Al-bearing stishovite has not been reported. In addition to the Al substitution, subducting slabs can contain a small amount of water in hydrous or nominally anhydrous minerals (NAMs) in the mantle. In multi-anvil apparatus experiments, Fourier-transform infrared spectroscopy (FTIR) analyses showed that Al-bearing stishovite crystals contain approximately 0.03–0.67 mol% H at 20–26 GPa and 1,473–2,073 K conditions (Litasov et al., 2007). The Al$^{3+}$ and/or H$^+$ incorporation in stishovite can reduce the post-stishovite transition pressure to the depth range more consistent with the seismic observations of the regional $V_S$ anomalies in the shallow lower mantle (Lakshtanov et al., 2007b; Umemoto et al., 2016). Although full elasticity of pure stishovite and post-stishovite and the effect of Al on the post-stishovite transition pressure have been relatively well investigated (Asahara et al., 2013; Karki et al., 1997; Lakshtanov et al., 2007b; Li et al., 1996; Shieh et al., 2002; Yang & Wu, 2014; Zhang et al., 2021), elasticity data of hydrated Al-bearing stishovite across the post-stishovite transition remain
largely unexplored (Bolfan-Casanova et al., 2009; Gréaux et al., 2016; Lakshtanov et al., 2007a). This is mainly due to the technical difficulty in measuring sound velocities and reliably deriving full elastic moduli \( C_{ij} \) of the stishovite crystal at high pressure (Zhang et al., 2021). Alternatively, high-pressure experimental results on Raman shifts of optic modes and equations of state (EOS) parameters across the post-stishovite transition can be used to evaluate full \( C_{ij} \) using Landau theory modeling (Carpenter et al., 2000). The full \( C_{ij} \) data can then be used to calculate sound velocities and other elastic parameters across the post-stishovite transition as a function of pressure.

In this study, we have measured Raman shifts of major optic modes and lattice parameters of two hydrated Al-bearing stishovite single crystals, \( \text{Al}_{1.3}\text{SiO}_2 \) (1.34 mol% Al and 0.55 mol% H) and \( \text{Al}_{2.1}\text{SiO}_2 \) (2.10 mol% Al and 0.59 mol% H), up to \( \sim70 \) GPa in high-pressure diamond anvil cells. The experimental data are modeled with a pseudoproper Landau theory in which some Landau parameters have been well constrained using a recent experimental elasticity study of stishovite at high pressure (Zhang et al., 2021). These combined experimental and modeling approaches allow us to determine full elastic properties of the Al,H-bearing stishovite, including \( C_{ij} \), adiabatic bulk and shear moduli \((k_c \text{ and } \mu)\), aggregate sound velocities \((V_g \text{ and } V_p)\), and Poisson’s ratio \(\nu\), across the post-stishovite transition at high pressure. Our results show that the post-stishovite transition occurs at 21.1 GPa in \( \text{Al}_{1.3}\text{SiO}_2 \) and 16.1 GPa in \( \text{Al}_{2.1}\text{SiO}_2 \), where the \( B_{ij} \) optic mode softens and the elastic moduli \( C_{11} \text{ and } C_{12} \) merge together. The full \( C_{ij} \) and sound velocities of hydrated Al-bearing stishovite and post-stishovite from high-pressure Raman and X-ray diffraction measurements are used to provide new constraints on Al/H-dependent post-stishovite transition and associated velocity changes at high \( P-T \). Assuming that subducted MORB materials contain 20 vol% stishovite with 1.3 mol% Al and 0.6 mol% H, our results show that the post-stishovite transition can exhibit a \( V_g \) reduction of \( -7(4)\% \). We have further modeled the \( V_g \) anomaly of the post-stishovite transition as a function of Al contents at high \( P-T \). These results are compared with regional seismic observations in some selected subduction zone settings including the Tonga slab. Our results provide new insights into the regional seismic \( V_g \) anomalies that can be explained by the hydrated Al-bearing post-stishovite transition from the top- to mid-lower mantle.

2. Experimental Details

Al,H-bearing stishovite crystals were synthesized at the Institute for Planetary Materials at Okayama University. Two starting samples were prepared by mixing silica powder of 99.99% purity with 10 wt% gibbsite \( \text{Al(OH)}_3 \) in run# 5K3302 and with 13 wt% gibbsite \( \text{Al(OH)}_3 \) in run# 1K2965. Each starting mixture was loaded into a platinum capsule of 4 mm in length and 2 mm in outer diameter. The sample assemblage in run# 5K3302 with a \( \text{LaCrO}_3 \) heater was compressed to 20 GPa and then heated to 1973 K for 16.5 hr in a 5000-ton Kawai-type multi-anvil apparatus. The assemblage in run# 1K2965 with the same type of heater was compressed to 19.2 GPa and heated to 1973 K for 7 hr using a 1,000-ton Kawai-type multi-anvil apparatus. Detailed information about the sample assemblage and apparatus conditions can be found in the literature (Okuchi et al., 2015; Xu et al., 2017). Stishovite crystals extracted from the Pt capsules are anhedral to subhedral in shape and are about tens to hundreds of micrometers in length under a few micrometers. A few crystals of approximately 100–200 μm in diameters were selected for compositional analysis using a JEOL Electron Microprobe (EPMA) and a Scanning Electron Microscopy with Energy Dispersive X-Ray Spectroscopy (SEM/EDS) in the Department of Geological Sciences at the University of Texas at Austin (UT Austin). Chemical mappings on Si, Al, and O elements show compositional homogeneities throughout the crystals (Figure S1 in Supporting Information S1). Quantitative results from Wavelength-Dispersive Spectroscopy (WDS) analysis show Al contents of 1.34(2) mol% (or 3.43(6) wt% \( \text{Al}_2\text{O}_3 \) averaged from 5 analyses) in the \( \text{Al}_{1.3}\text{SiO}_2 \) crystal from run# 5K3302 and 2.10(2) mol% (or 5.37(4) wt% \( \text{Al}_2\text{O}_3 \) averaged from 8 analyses) in \( \text{Al}_{2.1}\text{SiO}_2 \) from run# 1K2965 (Table S1 in Supporting Information S1). Other elements are below the detection limit of the analytical techniques used here.

Synchrotron X-ray diffraction (XRD) measurements are used to determine structures and lattice parameters of the crystals at the beamline 13-ID-D of the GSECARS, Advanced Photon Source (APS), Argonne National Laboratory. A few \( \text{Al}_{1.3}\text{SiO}_2 \) and \( \text{Al}_{2.1}\text{SiO}_2 \) crystals were polished down to approximately 10–15 μm thick platelets, and then loaded into a sample chamber in a diamond anvil cell with a pair of 300 μm flat culets. The sample chamber was made of a rhenium gasket with an initial thickness of 260 μm that was pre-indentend to ~32 μm thickness and subsequently a hole of 190 μm diameter was drilled in it. Au powder (Goodfellow; 99.95% purity)
of \( \sim 8 \times 10 \mu m^2 \) grain size was also loaded next to the crystals in the sample chamber and used as the pressure calibrant (Fei et al., 2007). Neon pressure medium was loaded into the sample chamber using the gas loading system in the Mineral Physics Laboratory, UT Austin. The neon medium provides a quasi-hydrostatic environment in the sample chamber within our investigated pressure range (Kingma et al., 1995). An incident X-ray beam with a wavelength of 0.3344 Å was focused down to a beam size of \( \sim 3 \times 3 \mu m^2 \) (FWHM) at the sample position where the diffracted signals were collected by a CdTe Pilatus 1M detector. During the data collection, the sample stage was rotated \( \pm 15^\circ \) about its vertical axis to cover as many reflection spots as possible. The collected images were further integrated into one-dimensional spectra using the DIOPTAS software (Prescher & Prakapenka, 2015). Pressure uncertainties were evaluated from the EOS of Au in the experiments.

High-pressure Raman measurements were performed using a Renishaw InVia Raman spectroscopy system at the Mineral Physics Laboratory, UT Austin. A pair of anvils with 300 μm flat culets and ultralow fluorescence background were selected for the experiments. Similar to the sample preparation in aforementioned XRD experiments, Al1.3-SiO2 and Al2.1-SiO2 platelets of 10–15 μm thick and \( \sim 20 \times 40 \mu m^2 \) grain size were loaded into a sample chamber with Ne pressure medium. A few ruby spheres were also loaded in the chamber and used as the pressure calibrant (Fei et al., 2007). The Raman system is equipped with a green excitation laser of 532 nm wavelength, a grating of 2400-line/mm, and a spectral resolution of 1.2 cm\(^{-1}\). The system was calibrated using the Raman peak of a reference Si crystal at 520 cm\(^{-1}\) before high-pressure measurements. Each Raman spectrum was collected using a 20X objective with a focused beam width of \( \sim 2–3 \mu m \), an exposure time of 15 s, and 20–30 accumulations. Pressure uncertainties of the experiments were evaluated from multiple ruby fluorescence measurements before and after each set of the Raman collection. Water contents in the crystals were also evaluated using unpolarized FTIR spectra taken in a Thermo Electron 6700 FTIR spectrometer with a connected FTIR Continuum microscope in the Department of Earth Sciences at the National Cheng Kung University. Raman spectra of the OH-stretching band regions of the Al,H-bearing stishovite crystals were also measured at ambient conditions.

### 3. Results

#### 3.1. Al and H Substitution in the Rutile-Type Stishovite

Combined results of FTIR, Raman, electron microprobe and XRD spectral measurements are useful to examine Al and H substitutions in hydrated Al-bearing stishovite crystal structure (Figure 1). Analysis of XRD spectra of the synthesized crystals reveals the tetragonal rutile-type crystal structure with \( \text{P4}_2\text/mnm \) space group at ambient conditions. Refined lattice parameters of the Al1.3-SiO2 crystal are \( a = 4.1963(8) \) Å, \( c = 2.6723(4) \) Å, and \( V = 47.06(2) \) Å\(^3\) while the Al2.1-SiO2 crystal displays \( a = 4.2025(9) \) Å, \( c = 2.6788(16) \) Å, and \( V = 47.31(2) \) Å\(^3\). Our results are consistent with the literature data in which the unit-cell volume of stishovite linearly expands with increasing Al content (Figure 1c; Lakshmanov et al., 2007b; Litasov et al., 2007). The lattice expansion can be mainly related to the coupled \( 2\text{Al}^{4+} \) and \( \text{O}_v^{2+} \) (oxygen vacancy) substitution for \( 2\text{Si}^{4+} \) in stishovite (Lakshmanov et al., 2007a). On the other hand, analysis of unpolarized FTIR and Raman spectra shows three major OH-stretching bands at \( \sim 2660, \sim 3140, \) and \( \sim 3410 \) cm\(^{-1}\), consistent with literature data (Figures 1a and 1b; Litasov et al., 2007). The strongest FTIR absorption band at \( 3140 \) cm\(^{-1}\) is also extremely intense in Raman measurements, revealing itself as an active FTIR and Raman mode. This is also the case for the modes at 2660 and 3410 cm\(^{-1}\). The occurrence of the bands has been explained to be indicative of the coupled \( \text{Al}^{3+} + \text{H}^+ \) and/or pure \( 4\text{H}^+ \) substitution for \( \text{Si}^{4+} \) in the structure, which are also expected to contribute to the expansion of the lattice (Nisr et al., 2017; Spektor et al., 2011). The water content \( C_{\text{OH}} \) of the crystals in the unpolarized spectra can be determined using a calibration method by Paterson (1982):

\[
C_{\text{OH}} = \frac{X_i}{150\gamma} \int k(\tilde{\nu}) \frac{k(\nu)}{(3780 - \nu)} d\nu
\]

where \( X_i \) is the density factor, \( X_i = 9/\rho \times 10^6 \), with the density as 4,237 g/l and 4,211 g/l for Al1.3-SiO2 and Al2.1-SiO2, respectively; \( \gamma \) is the orientation factor which is set as 1/3 for the unpolarized measurements; \( k(\nu) \) is an absorption in cm\(^{-1}\) at each wavenumber \( \nu \) in cm\(^{-1}\). After subtracting the background and normalizing the sample thickness to 1 cm, the water contents in Al1.3-SiO2 and Al2.1-SiO2 crystals are determined as 0.55(11) mol% H (or 0.25(5) wt% H\(_2\)O) and 0.59(11) mol% H (or 0.27(5) wt% H\(_2\)O), respectively. Together with chemical
analysis results, the molar ratios of Al/H in these crystals are thus 2.4(7):1 and 3.5(8):1. These numbers are close to 2:1 and 3:1 ratio, but much larger than 1:1 ratio for the coupled Al$^{3+} + H^+$ substitution mechanism proposed previously (Pawley et al., 1993) (Figure 1d). These indicate that 2Al$^{3+} + O_v^{2+} \leftrightarrow 2Si^{4+}$ mechanism is predominant in our Al,H-bearing stishovite crystals to expand the lattice, while the Al$^{3+} + H^+ \leftrightarrow Si^{4+}$ mechanism can help facilitate water incorporation into stishovite.

3.2. High-Pressure Raman Shifts of Major Optic Modes Across the Post-Stishovite Transition

Analyses of the Raman spectra of the crystals at ambient conditions show four intense optic Raman bands at 226, 583, 748, and 960 cm$^{-1}$ in Al1.3-SiO$_2$ and at 224, 579, 744, and 957 cm$^{-1}$ in Al2.1-SiO$_2$. After taking the Al substitution effects into account, these peaks can be assigned to $B_{1g}$, $E_g$, $A_{1g}$, and $B_{2g}$ modes of the rutile-type stishovite, respectively (Kingma et al., 1995). The $B_{1g}$, $E_g$, and $A_{1g}$ peaks can be well detected at high pressure, but the $B_{2g}$ mode was blocked by the background of the diamond anvil (Tables S2–S4 in Supporting Information). Raman shifts of $E_g$ and $A_{1g}$ modes increase with increasing pressure whereas the Raman shifts of the $B_{1g}$ mode decrease with increasing pressure (Figure 2). The trends and slopes of these Raman shifts are consistent with those in pure SiO$_2$ stishovite at high pressure (Kingma et al., 1995; Zhang et al., 2021). Crossing into the CaCl$_2$-type post-stishovite phase, the $B_{1g}$ and $A_{1g}$ evolve into two $A_g$ modes but splitting of $E_g$ mode into $B_{2g}$ and $B_{3g}$ modes was not observed due to background of the diamond anvil. Raman shifts of the $A_g$ modes in the post-stishovite phase increase with increasing pressure, but the slope is shallower than that in pure SiO$_2$ stishovite (Figure 2c). Most importantly, the pressure-dependence of the stishovite’s $B_{1g}$ mode becomes positive in the
post-stishovite’s $A_g$ mode after the post-stishovite transition. A satellite band, denoted as $A_g^*$, in the Al$_{1.3}$-SiO$_2$ crystal occurs between 21.1 and 36.5 GPa (Figures 2a and 2c) with Raman shift behavior similar to the $A_g$ mode, but the kink occurs at approximately 28 GPa. The occurrence of the satellite peak may be due to local clusters of Al-poor regions where the local domains can resist the ferroelastic transition to a higher pressure. This phenomenon across the ferroelastic transition has been reported in other binary systems (Salje, 1990).

### 3.3. Lattice Parameters Across the Post-Stishovite Transition

Analysis of the high-pressure XRD spectra from Al$_{1.3}$-SiO$_2$ and Al$_{2.1}$-SiO$_2$ crystals shows 10–15 reflections in the tetragonal stishovite phase with 2θ ranging from 6° to 24° (Figures 3a and 3b; Tables S5 and S6 in Supporting Information S1). The analyzed lattice parameters indicate that lengths of $a$ and $c$ axis and unit-cell volume ($V$) decrease with increasing pressure with slopes consistent with those in pure-endmember stishovite (Figures 3c and 3d). With increasing pressure, some representative diffraction peaks in the tetragonal structure split into pairs of orthorhombic (211 and 121) and (311 and 131) reflections, respectively, in Al$_{1.3}$-SiO$_2$ crystal (Figure 3a). Similarly, splitting of tetragonal 210, 211, 310, 311, 320, 410, 411, and 420 reflections was observed in Al$_{2.1}$-SiO$_2$ crystal (Figure 3b). These mean that the $a$-axis of the tetragonal stishovite splits into $a$- and $b$-axis of orthorhombic post-stishovite at high pressure. Axial and bulk incompressibilities of the stishovite and post-stishovite phases at high pressure were further evaluated using the Birch-Murnaghan EOS (Birch, 1947; Table S7 in Supporting Information S1). Isothermal bulk modulus ($K_{T0}$) of Al$_{1.3}$-SiO$_2$ and Al$_{2.1}$-SiO$_2$ crystals at ambient conditions is lower than that in pure SiO$_2$ stishovite, but higher than that in pure SiO$_2$ post-stishovite. These indicate that the Al and H substitution softens the tetragonal structure in stishovite but stiffens the orthorhombic structure in post-stishovite.
4. Discussion

4.1. Landau Theory Modeling of the Elasticity Across the Post-Stishovite Transition

Our high-pressure Raman and XRD results are used to derive full $C_{ij}$ and sound velocities of the stishovite and post-stishovite phases. We use a pseudoproper-type Landau free energy expansion, where the order parameter $Q$ is related to the soft $B_{1g}$ optic mode and is coupled bilinearly with the symmetry-breaking spontaneous strain (Carpenter et al., 2000). In the modeling, a number of Landau parameters need to be well evaluated in order to reliably derive the full elastic moduli. These parameters include $A_{*}$, critical pressure ($A_{*}C_{A_{*}}$), bare elastic moduli ($A_{0}$), pressure derivatives of $A_{0}$ ($A_{0}'$), and normal Landau coefficients ($A_{*}$ and $A_{0}$). To start with, the intersection of the two linear fits to the squared Raman shifts of the $B_{1g}$ and $A_{g}$ modes as a function of pressure gives the $A_{*}C_{A_{*}}$ value at 21.1(6) GPa for Al$_{1.3}$SiO$_2$ and at 16.1(4) GPa for Al$_{2.1}$SiO$_2$ (Figure 4a). Extrapolation of the $B_{1g}$ linear fit to zero Raman shift yields the $A_{*}$ value where the optic mode becomes imaginary. Additionally, the $C_{0}$ can be calculated from literature $C_{0}$ data of stishovite at ambient conditions after taking into account of the linear Al effect on the $C_{0}$ in stishovite (Lakshtanov et al., 2007a). Since the pressure-dependent slopes for Raman shifts and lattice parameters are very similar in Al,H-bearing and pure SiO$_2$ stishovite (Figures 2c, 3c, and 3d), the $C_{ij}$ slope, the pressure derivatives of $C_{ij}$ ($C_{ij}'$), of the experimentally-determined values for pure SiO$_2$ endmember in a recent study can be used for the Al,H-bearing stishovite (Zhang et al., 2021). The exception here is for the $C_{ii}$ and $C_{ij}$ that can be affected by the shear softening and the transition.
pressure such that these two parameters for the ALH-bearing stishovite need to be evaluated in the modeling. Moreover, the coupling coefficients \( \lambda_i \) and \( \lambda_b \) are also set to those in the pure SiO2 endmember because they are related to the spontaneous strains \( e_s \) and \( e_t \) and \( e_b \) that remain zero in the post-stishovite phase regardless of the Al and H contents due to the nature of the ferroelastic transition (Carpenter et al., 2000). In short, six parameters (coupling coefficients \( \lambda_i \) and \( \lambda_b \), Landau coefficients \( a \) and \( b \), \( C_{ij}^0 \) and \( C_{ij}^0 \)) are evaluated in our modeling using the Al and H dependent spontaneous strains \( e_s \), \( e_t \), and \( e_b \) at high pressures that can be calculated from the lattice parameters (Figure 4b):

\[
e_1 = \frac{a_{P_{st}} - a_{S}}{a_{S}}, \quad e_2 = \frac{b_{P_{st}} - b_{S}}{b_{S}}, \quad e_3 = \frac{c_{P_{st}} - c_{S}}{c_{S}}
\]

where \( a_{P_{st}}, b_{P_{st}}, \) and \( c_{P_{st}} \) are lattice parameters of post-stishovite (\( P_{st} \)) at high pressure; \( a_{S} \) and \( c_{S} \) are the extrapolated lattice parameters of stishovite (\( S \)) at the same pressure. With all these Landau parameters determined (Table 1), the full set of \( C_{ij} \) of the stishovite and post-stishovite phases at high pressure can be calculated using the following expressions (Carpenter et al., 2000):

\[
C_{11} = C_{11}^0 - (4\lambda_1^2Q^2 + \lambda_2^2 + 4\lambda_1\lambda_2Q)\chi
\]

\[
C_{22} = C_{11}^0 - (4\lambda_1^2Q^2 + \lambda_2^2 - 4\lambda_1\lambda_2Q)\chi
\]

\[
C_{33} = C_{33}^0 - 4\lambda_3^2Q^2\chi
\]

\[
C_{12} = C_{12}^0 - (4\lambda_1^2Q^2 - \lambda_2^2)\chi
\]

\[
C_{13} = C_{13}^0 - (4\lambda_1\lambda_3Q^2 + 2\lambda_2\lambda_3Q)\chi
\]

\[
C_{23} = C_{13}^0 - (4\lambda_1\lambda_3Q^2 - 2\lambda_2\lambda_3Q)\chi
\]

\[
C_{44} = C_{44}^0 + 2\lambda_4Q
\]

\[
C_{55} = C_{44}^0 - 2\lambda_4Q
\]

\[
C_{66} = C_{66}^0 + 2\lambda_6Q^2
\]

where \( \chi \) is the susceptibility and \( Q \) is the order parameter as

\[
\chi = \begin{cases} 
1/\left[a\left(P - P_c\right)\right], & \text{if } P \leq P_c^* \\
1/\left[2ab\left(P_c^* - P\right)/b^* + a\left(P_c^* - P\right)\right], & \text{if } P > P_c^*
\end{cases}
\]

\[
Q = \begin{cases} 
0, & \text{if } P \leq P_c^* \\
\sqrt{a\left(P_c^* - P\right)/b^*}, & \text{if } P > P_c^*
\end{cases}
\]

with the renormalized Landau coefficient \( b^* \) as

\[
b^* = b - 2\left[\frac{\lambda_1^2\left(C_{11}^0 + C_{12}^0\right) + 2\lambda_1\lambda_3C_{13}^0 - 4\lambda_1\lambda_3C_{13}^0}{C_{33}^0\left(C_{11}^0 + C_{12}^0\right) - 2C_{13}^0}\right]
\]

Standard deviations of the \( C_{ij} \)'s can be estimated using the equation for the standard error propagation (refer to Text S1 in Supporting Information S1 for details).
We further calculate $AASA$ and $ASAASA$ from our modeled $C_{ij}$ values using Voigt–Reuss–Hill averaging scheme at high pressure (Hill, 1952). With $ASAASA$ determined from EOS parameters (Table S7 in Supporting Information S1), the $VS$ and $VP$ values of stishovite and post-stishovite phases at each given pressure are calculated using the following equations:

$$VP = \sqrt{(K_S + \frac{4}{3} \mu) / \rho}, \quad VS = \sqrt{\mu / \rho}$$  \hspace{1cm} (15)

The Poisson’s ratio $\nu$, a key seismic parameter reflecting the $VP$ and $VS$ ratio, is also calculated using the following equation:

$$\nu = \frac{1}{2} \left( \frac{VP}{VS} \right)^2 - 1$$  \hspace{1cm} (16)

4.2. Al and H Effects on the Post-Stishovite Transition Boundary

The post-stishovite transition boundary influenced by the Al and/or H substitutions at relevant mantle $P$-$T$ conditions can be of direct relevance to our understanding of the depth-dependent distributions of the regional seismic $VS$ anomalies in the lower mantle as discussed in the introduction. Therefore, we have compared our results with literature data to better evaluate the transition boundary as a function of Al and/or H contents. Based on...

| Compositions | Al1.3-SiO$_2$, 0.7 mol% H$^+$ | Al2.1-SiO$_2$, 0.8 mol% H$^+$ | SiO$_2$, 0.004 mol% H$^+$ |
|--------------|-------------------------------|-----------------------------|--------------------------|
| $P_C$, GPa   | 21.1(6)                       | 16.1(4)                     | 55.0(10)                 |
| $(P_C - P_C^*)$, GPa | 105.7(38) | 134.3(65) | 55.2(10) |
| $a$          | $-0.0512(49)$                 | $-0.0467(45)$               | $-0.0501(29)$            |
| $b$          | 10.5(12)                      | 10.6(14)                    | 11                       |
| $\lambda_4$, GPa | 60.5            | 78.5                       | 27.61                    |
| $\lambda_5$, GPa | 12.6(13)           | 12.2(11)                   | 16.79(92)                |
| $\lambda_6$, GPa | 18.94                     | 18.94                      | 18.94(31)                |
| $\lambda_7$, GPa | 15.15                     | 15.15                      | 15.15(22)                |
| $C^0_{110}$, GPa | 999                          | 1302                        | 592.3                    |
| $C^0_{11}$, GPa | 10.0(9)                      | 9.5(9)                      | 10.80(47)                |
| $C^0_{120}$, GPa | $-375$                      | $-693$                      | 57.9                     |
| $C^0_{12}$, GPa | 9.9(7)                       | 10.4(8)                     | 8.81(63)                 |
| $C^0_{130}$, GPa | 190.6                       | 189.2                       | 193.0                    |
| $C^0_{13}$, GPa | 2.91                         | 2.91                        | 2.91(27)                 |
| $C^0_{33}$, GPa | 743.5                        | 734.1                       | 760.2                    |
| $C^0_{33}$, GPa | 7.07                         | 7.07                        | 7.07(48)                 |
| $C^0_{44}$, GPa | 246.7                        | 238.2                       | 261.6                    |
| $C^0_{44}$, GPa | 3.18                         | 3.18                        | 3.18(5)                  |
| $C^0_{60}$, GPa | 295.2                        | 281.4                       | 319.7                    |
| $C^0_{66}$, GPa | 5.60                         | 5.60                        | 5.60(13)                 |

Note. See the main text for the meaning and references of Landau parameters listed in the first column. Numbers in parentheses represent ±1σ uncertainties.

We further calculate $K_S$ and $\mu$ from our modeled $C_{ij}$ values using Voigt–Reuss–Hill averaging scheme at high pressure (Hill, 1952). With $\rho$ determined from EOS parameters (Table S7 in Supporting Information S1), the $V_P$ and $V_S$ values of stishovite and post-stishovite phases at each given pressure are calculated using the following equations:

$$VP = \sqrt{(K_S + \frac{4}{3} \mu) / \rho}, \quad VS = \sqrt{\mu / \rho}$$  \hspace{1cm} (15)

The Poisson’s ratio $\nu$, a key seismic parameter reflecting the $VP$ and $VS$ ratio, is also calculated using the following equation:

$$\nu = \frac{1}{2} \left( \frac{VP}{VS} \right)^2 - 1$$  \hspace{1cm} (16)

4.2. Al and H Effects on the Post-Stishovite Transition Boundary

The post-stishovite transition boundary influenced by the Al and/or H substitutions at relevant mantle $P$-$T$ conditions can be of direct relevance to our understanding of the depth-dependent distributions of the regional seismic $VS$ anomalies in the lower mantle as discussed in the introduction. Therefore, we have compared our results with literature data to better evaluate the transition boundary as a function of Al and/or H contents. Based on...
Figure 5. Post-stishovite phase transition boundary influenced by Al content in stishovite. (a) The post-stishovite transition pressure as a function of the Al content in mol% at 300 K. The dashed line is the best polynomial fit to our data using 55 GPa as the transition pressure of the pure SiO$_2$ by Zhang et al. (2021). The red shaded area in Al1.3-SiO$_2$ represents a pressure region where the stishovite and post-stishovite phases coexist (see Figures 2a and 2c). Literature results are also shown for comparison (Andraut et al., 2003; Bolfan-Casanova et al., 2009; Buchen et al., 2018; Lakshtanov et al., 2007b; Zhang et al., 2021). (b) Post-stishovite transition at high P-T conditions. A Clapeyron slope of 65 K/GPa is used for the post-stishovite transition (Fischer et al., 2018), where stishovite contains 0 (black), 1 (red), 2 (green), and 3 (blue) mol% Al, respectively. The horizontal bar at the bottom right indicates the coexistence range of the Al,H-bearing stishovite and post-stishovite phases, which is estimated from the coexistence of the $A_1$ and $A_2$ modes in Al1.3-SiO$_2$ (Figures 2a and 2c). A typical normal mantle geotherm (Katsura et al., 2010) and a cold slab geotherm that is 500 K colder than a typical normal mantle (Tan et al., 2010; Tan et al., 2002), the post-stishovite transition is expected to occur at 740 km depth with 3 mol% Al and at 1,250 km depth with 1 mol% Al (Figure 5b). We should note that since the oceanic crust is thin and mainly exists on the surface of the subduction slabs, our cold-slab geotherm assumption, that is, 500 K colder than the surrounding mantle, should be taken as an upper bound of the temperature conditions.

### 4.3. Al and H Effects on the Sound Velocities Across the Post-Stishovite Transition

Our Landau modeling results provide full elastic moduli of the (Al,H)-bearing stishovite crystals across the post-stishovite transition at high pressure (Figure 6; refer to Tables S8 and S9 in Supporting Information S1 for numerical values of $C_{ij}$). Examinations of the pressure-dependent $C_{ij}$ in the Al1.3-SiO$_2$ and Al2.1-SiO$_2$ crystals show that they are overall consistent with that of pure SiO$_2$ (Zhang et al., 2021), but the slopes across the transition are quite different. The (Al,H)-bearing stishovite crystals display softer $C_{11}$ and stiffer $C_{12}$, approaching the transition than the pure SiO$_2$, stishovite phase. These lead to the convergence of $C_{11}$ and $C_{12}$ at a lower $P_C^*$ in the (Al,H)-bearing system. We should note that the $(C_{11}-C_{12})/2$ constant, which reflects the response of a crystal to deformation caused by shear stress along the [110] direction, is expected to vanish at the transition (Figure 6a).

Similarly, the deviations between $C_{12}$ and $C_{22}$ and between $C_{11}$ and $C_{23}$ in the post-stishovite phase become larger (Figures 6a and 6b). In addition, our results show an enhanced reduction in the shear modulus and sound velocities (Figures 6c and 6d): the transition correlates with 49% $\mu$ reduction, 29% $V_S$ reduction, and 12% $V_P$ reduction as compared with reductions of 45% in $\mu$, 26% in $V_S$, and 10% in $V_P$ in pure SiO$_2$ post-stishovite transition (Zhang et al., 2021).
4.4. Velocity Profiles of Subducted MORB Across the Post-Stishovite Transition in the Lower Mantle

The post-stishovite transition is known to occur in the subducted MORB such that sound velocity of the MORB materials can be useful in deciphering seismic results along subducting zone regions in the lower mantle. In our modeling to evaluate the effects of the post-stishovite transition on velocity profiles, we used elasticity of individual mineral phases in an aggregate with MORB composition along the aforementioned cold-slab geotherm. The mineralogy in the selected MORB composition contains 20 vol% stishovite, 30 vol% CF, 30 vol% Bgm, and 20 vol% CaPv in the lower mantle (Ishii et al., 2019). Thermoelastic parameters of these mineral phases, except CaPv, in our modeling are taken from this study, Zhang et al. (2021), and Xu et al. (2008). We should note that Xu et al. (2008) determined these parameters using previous elasticity data at high P-T (refer to Table S10 in Supporting Information S1 for details; Akaogi et al., 1999; Fei & Ahrens, 1995; Fiquet et al., 2000; Funamori et al., 1998; Kiefer et al., 2002; Liu et al., 1999; Murakami et al., 2003; Shim & Duffy, 2000; Sinogeikin et al., 2004; Smyth & McCormick, 1995; Wentzcovitch et al., 2004). On the other hand, thermoelastic parameters for CaPv are obtained by refitting combined elasticity data sets from Gréaux et al. (2019) and Sun et al. (2016) (Table S10 in Supporting Information S1). We should note that the CaPv data by Thomson et al. (2019) are not used here because they measured sound velocities at a nearly constant pressure such that some thermoelastic parameters cannot be reliably constrained such as pressure derivatives of $K_S$ and $\mu$. Mie-Grüneisen EOS and finite-strain theory are then used to calculate $\rho$, $K_S$, and $\mu$ of each mineral phase in the MORB mineralogy along a cold subducting slab based on the following equations (Stixrude & Lithgow-Bertelloni, 2005):

$$P = 3K_{T0}f(1 + 2f)^{3/2} \left[ 1 + \frac{3}{2}(K'_{T0} - 4) f \right] + \gamma p \Delta \delta$$

(17)

$$K_S = (1 + 2f)^{3/2} \left[ K_{SO} + (3K_{SO}K'_{SO} - 5K_{SO}) f + \frac{27}{2} (K_{SO}K'_{SO} - 4K_{SO}) f^2 \right]$$

$$+ (\gamma + 1 - q)\gamma p \Delta \delta - \gamma^2 p \Delta (C_T)$$

(18)
\[
\frac{2}{3} - 5a_1 - 18t_t = -12 + \frac{S}{\mu_0 a_1} \quad \text{for the MORB}
\]

2013 is the width of the phase transition in GPa. Fitting our modeled
are internal
2021 is the maximum shear modulus softening in GPa,
and \( a_1 = 14.7(1) \text{ GPa} \) in Al1.3-SiO
\( a_1 = 13.9(2) \text{ GPa} \) in Al2.1-SiO
\( a_1 = -152.4(9) \) is a constant; \( \Omega \) and \( C_V \) are internal
and isochoric heat capacity, respectively, which can be calculated
using the Debye model; \( K'_{SO} \) and \( \mu_0 \) are the first-order pressure derivative
of \( K_{SO} \) and \( \mu_0 \), respectively; \( \eta_S \) is the first-order shear strain derivative of
\( \gamma, \eta_S = -\gamma + (2f + 1)(a_1 + a_2 f) / \left( 1 + a_1 f + \frac{1}{2} a_2 f^2 \right) \); \( \Delta \) means the difference
between high temperature and 300 K; the subscript ‘0’ denotes the ambient
conditions.

We should note that the finite-strain model cannot be applied to evaluate
the shear softening feature across the post-stishovite ferroelastic transition at
high \( P-T \) conditions. Therefore, in addition to the finite-strain modeling, we have
evaluated the shear modulus softening, \( \Delta \mu \), across the transition at high
\( P-T \) using the following equations (Helffrich et al., 2018):

\[
\Delta \mu = A_0 \left( 1 - \frac{2}{\pi} \arctan \left[ \frac{P - P_0(T)}{w} \right] \right)^2
\]

\[
P_0(T) = P_c^0 + s(T - 300)
\]

where \( A_0 \) is the maximum shear modulus softening in GPa, \( P_0(T) \) is the transition
pressure in GPa at \( T \) in K with a Clapeyron slope \( s \) of 1/65 GPa/K, and
\( w \) is the width of the phase transition in GPa. Fitting our modeled \( \mu \)
across the post-stishovite transition at 300 K with Equations 20 and 21 yields
\( A_0 = -148.4(7) \) GPa and \( w = 14.7(1) \) GPa in Al1.3-SiO
\( A_0 = -152.4(9) \) GPa and \( w = 13.9(2) \) GPa in Al2.1-SiO
(Figure 6c). After obtaining results from these aforementioned modeling efforts, \( \rho, K_s, \) and \( \mu \) for the MORB
mineralogy are calculated using the Voigt-Reuss-Hill scheme and volume
ratios of the minerals to derive the \( V_P \) and \( V_S \) profiles of the aggregates in
subducted MORB materials in the lower mantle (Figure 7) (Hill, 1952; Ishii
et al., 2019).

5. Geophysical Implication

The anomalous elastic properties of stishovite across the second-order phase transformation have important implications for the interpretation of seismological observations. The large velocity contrast between the stishovite near the phase transformation and co-existing minerals implies that there will be substantial seismic wave scattering at a boundary between stishovite-rich and stishovite-poor materials (Figure 7). First, for an obvious reason, the impact of stishovite on seismological observations depends on the amount of stishovite. For a typical lower mantle, stishovite exists only in regions occupied by subducted oceanic crust. Stishovite occupies approximately 20% in a typical oceanic crust subducted into the lower mantle (Ishii et al., 2019), whereas once subducted crust undergoes partial melting the amount of stishovite will increase substantially (Amulele et al., 2021). Second, since large velocity contrast (particularly in \( V_S \)) occurs at or near the depth of the second-order transformation, we expect to see the influence of stishovite in the depth corresponding to the depth of the phase transformation. Our and early experimental studies show that the depth at which the post-stishovite transition occurs strongly depends on the \( Al_2O_3 \) content ranging from ~800 to 1,600 km (Figure 5; Bolfan-Casanova et al., 2009; Lakshtanov et al., 2007b). The \( Al_2O_3 \) content in MORB materials ranges from ~4.3 to 8.1 mol% (Gale et al., 2013), which in turn affects
6. Conclusion

We have studied the vibrational Raman modes and lattice parameters of two ALH-bearing stishovite crystals, Al1.3-SiO$_2$ with 0.55 mol% H and Al2.1-SiO$_2$ with 0.59 mol% H, across the post-stishovite transition at high pressure. The experimental results are used to evaluate the Al and H substitutional effects on the post-stishovite phase boundary and the elasticity across the post-stishovite transition. Landau theory modeling of the experimental data is used to derive the transition pressure and full elasticity across the transition, where the softening of the $V_S$ mode becomes the hardening mode, the $a$ axis splits into the $a$ and $b$ axis, the $(C_{11}-C_{12})/2$ approaches zero, and the $V_g$ displays $-29\%$ softening. The Al and H incorporation reduces the transition pressure to 21.1 GPa in Al1.3-

the amount of Al in natural stishovite. Considering MORB materials with a typical $\sim 6.8$ mol% Al, stishovite is expected to contain $\sim 1.3$ mol% Al from 800 to 1,600 km depth (Figure S2 in Supporting Information S1).

Indeed, seismic wave scattering is often reported in regions linked to subduction zones from top- to mid-lower mantle. These subduction regions include South America (Haugland et al., 2017), Tonga (Kaneshima, 2013, 2018, 2019; Vinnik et al., 2001), Mariana (Kaneshima & Helffrich, 1999; Niu et al., 2003), and Japan sea (Li & Yuen, 2014; Niu, 2014). The magnitudes of the seismically-observed $V_S$ anomalies are generally consistent with our modeled maximum $V_S$ anomaly ($dV_{S,max}$) of 7–8(+4)% in MORB with 20% silica undergoing the post-stishovite transition (Figure 8a). Seismic observations also show that the number of these anomalies decreases with depth and the majority of these seismic scatterers ($\sim 85\%$) occurs above 1,600 km depth (Kaneshima, 2013, 2018, 2019). These observations can be interpreted as a result of the Al-dependent post-stishovite transition in subducted MORB materials as well as the broad $V_g$ reduction across the ferroelastic transition (Figure 8b).

Our results can also have implications to our understanding of the water circulation and storage in the deep mantle. MORB materials contain some water due to the hydrothermal processes. The subduction of MORB materials can bring a certain amount of water into the mantle through hydrogen dissolved in NAMs. Stishovite is one of the NAMs and can accommodate a certain amount of water in its lattice along the subduction processes (Lin et al., 2019; Litasov et al., 2007; Ohtani, 2020). As the slabs reach the 660-km boundary layer in some subduction regions, dehydration-induced partial melting can occur in the shallow lower mantle (Liu et al., 2016; Schmandt et al., 2014) and produce Al-bearing stishovite with approximately 700 wt ppm H$_2$O (Amulele et al., 2021). Our ALH-bearing stishovite can contain 0.25 and 0.27 wt% H$_2$O with an Al:H ratio close to 2:1 (Figure 1d). Using 2:1 for the Al:H ratio in natural stishovite in a typical MORB composition, stishovite with 1.3 mol% Al$_2$O$_3$ would contain approximately 0.65 mol% H (or 0.3 wt% H$_2$O) in the upper part of the lower mantle. The 0.3 wt% H$_2$O in stishovite is significantly larger than the water solubility of $\sim 0.1$ wt% in other MORB components such as Bgm and NAL phase (Fu et al., 2019; Wu et al., 2016), making the ALH-bearing stishovite a plausible water carrier along the subduction slabs into the lower mantle.

Previous studies have shown that hydration in stishovite can significantly enhance its electrical conductivity by two orders of magnitude at 12 GPa and high temperature (Yoshino et al., 2019). Electromagnetic observations of high electrical conductivity regions along circum-Pacific subducting slabs in the shallow lower mantle (Kelbert et al., 2009) may be interpreted as a result of the presence of hydrated silica-rich materials.

Figure 8. Seismic observations and mineral physics modeling of the depth-dependent $V_S$ anomalies ($dV_S$) in the lower mantle. (a) $dV_S$ observations of regional seismic $V_S$ anomalies around subducting slabs at various depths are plotted as open circles. 20 vol% stishovite in a subducted MORB composition is used in our mineral physics model to account for the maximum $V_S$ anomaly ($dV_{S,max}$) across the post-stishovite transition shown as solid circles. The $dV_{S,max}$, in % is calculated using the formula of $(V_{S,MORB}-V_{S,cold slab})/V_{S,cold slab} \times 200$, where the $V_{S,cold slab}$ value is 1% higher than the $V_S$ of PREM at the same depth (Dziewonski & Anderson, 1981) (Figure 7b). Literature data for seismic observations include Haugland et al. (2017), Kaneshima (2018, 2019), Vinnik et al. (2001), Kaneshima (2013), Kaneshima and Helffrich (1999), Niu et al. (2003), Niu (2014), and Li and Yuen (2014). Note that some of these studies have only reported lower bound of the $V_S$ anomaly (Kaneshima, 2013, 2018; Kaneshima & Helffrich, 1999). (b) Depth-longitude schematics for the seismic $dV_S$ anomalies and the post-stishovite transition along the Tonga subduction region. The color shaded area represents the post-stishovite transition region scaled with the Al content in a color scale shown on the top right. Reported seismic $V_S$ anomalies (red open circles) with different latitudes in the Tonga region are projected onto the two-dimensional schematic (Kaneshima, 2009, 2013, 2018, 2019; Kaneshima & Helffrich, 2010). The geometry and position of the Tonga subducting slab are drawn according to previous seismic images (Fukao & Obayashi, 2013).
SiO₂ and 16.1 GPa in Al₂1-SiO₂⁴. We have modeled high P-T phase boundary and elasticity of stishovite and post-stishovite for a MORB mineralogy with 20 vol% stishovite. For a typical MORB composition where stishovite is expected to contain 1.3 mol% Al, the post-stishovite transition can cause for −7(4)% dV_P,max in subducted MORB at 1064 km depth. These results help explain depth-dependent V_p anomaly distributions of some regional small-scale scatterers especially for the S-to-P scattering along the Tonga subduction region. The Al,H-bearing stishovite can also accommodate approximately 0.3 wt% H₂O via the coupled substitution mechanism of Al¹⁺ + H⁺ ↔ Si⁴⁺ in the upper part of the lower mantle. The lattice-bonded water is expected to remain stable in the post-stishovite phase. The water in stishovite and post-stishovite phases could affect electrical conductivity of silica-rich materials in the region.

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Conflict of Interest
The authors declare no conflicts of interest relevant to this study.

Data Availability Statement
EPMA results are listed in Table S1 in Supporting Information S1. Raman data for Figure 2 are available in Tables S2–S4 in Supporting Information S1. XRD data for Figure 3 are available in Tables S5–S7 in Supporting Information S1. Numerical values of the modeled C_p for Figure 6 are listed in Tables S8 and S9 in Supporting Information S1. Thermoelastic parameters used in the modeling are listed in Table S10 in Supporting Information S1. All these data can also be downloaded online (https://zenodo.org/record/6391581)
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