Equation of State and Spin Crossover of (Al, Fe)-Phase H

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Abstract

The transport of hydrogen into Earth's deep interior may have an impact on lower mantle dynamics as well as on the seismic signature of subducted material. Due to the stability of the hydrous phases δ-AlOOH (delta phase), MgSiO$_3$(OH)$_2$ (phase H), and ε-FeOOH at high temperatures and pressures, their solid solutions may transport significant amounts of hydrogen as deep as the core-mantle boundary. We have constrained the equation of state, including the effects of a spin crossover in the Fe$^{3+}$ atoms, of (Al, Fe)-phase H and ε-(Al, Fe)-phase H. The changes in spin state of Fe$^{3+}$ in (Al, Fe)-phase H result in a significant decrease in bulk sound velocity and occurs over a different pressure range (48–62 GPa) compared with δ-(Al, Fe)-phase H (32–40 GPa). Changes in axial compressibilities induce a decrease in the compressibility of hydrogen bonds in (Al, Fe)-phase H over 30 GPa, which may be associated with hydrogen bond symmetrization. The formation of (Al, Fe)-phase H in subducted oceanic crust could contribute to seismic waves in the mid-lower mantle (1,000–1,550 km). Accumulation of 1–4 wt.% (Al, Fe)-phase H could reproduce some of the seismic signatures of low, low seismic-velocity provinces. Our results suggest that changes in the electronic structure of phases in the (δ-AlOOH)-(ε-FeOOH) solid solution are sensitive to composition and that the presence of these phases in subducted oceanic crust could be seismically detectable throughout the lower mantle.

Plain Language Summary

Hydrogen can be transported into the interior of the Earth by phases which contain hydrogen in their crystal structure. Interpretation of measured seismic velocities relies on understanding the elastic properties of minerals, including their equation of state. In this study, we use X-ray diffraction and Mössbauer spectroscopy to constrain the equation of state for a particular hydrous phase known as (Al, Fe)-phase H and understand pressure-induced related effects due to changes in the electronic structure of Fe atoms. Our results imply that only a small amount of this phase needs to be transported to the deep mantle to reproduce observed seismic velocities at the edges of large structures known as low seismic-velocity provinces. The presence of (Al, Fe)-phase H in subducted oceanic crust may also contribute to the scattering of seismic waves in shallower regions of Earth's interior.

1. Introduction

In Earth's mantle, the volatile element hydrogen is incorporated into minerals as point defects in nominally anhydrous minerals and in the crystal structures of hydrous minerals (e.g., Bell & Rossman, 1992; Bolfan-Casanova, 2005; Litasov & Ohtani, 2003; Ohtani, 2015; Rossman, 1996). Transport of volatiles in minerals as part of subducted lithosphere results in cycling of hydrogen between Earth's surface and interior and places important constraints on the chemical and dynamic evolution of the Earth (Crowley et al., 2011; Nakagawa & Tackley, 2015; Parai & Mukhopadhyay, 2018). The presence of hydrogen in mantle minerals has been shown to affect the speed at which seismic waves propagate through the material and alter the properties of key seismic discontinuities in the mantle (Buchen et al., 2018; Jacobsen et al., 2010; Zhou et al., 2022). Additionally, the release of hydrogen from subducted lithosphere as a result of mineral reactions can affect mantle dynamics by the depression of solidus temperatures and partial melt formation (i.e., arc volcanism), reductions in mantle viscosity, or can result in metasomatic reactions (e.g., Palot et al., 2016; Pearson et al., 2014; Tschauner et al., 2018).
While mantle convection models predict a diverse set of possible slab dynamics in the mantle transition zone, these models often agree that subducting slabs can descend through the abrupt change in density at 670 km depth and eventually accumulate at the core-mantle boundary (Brandenburg & Van Keken, 2007; Tan et al., 2011). Regions of positive seismic velocity perturbation, which are inferred to be cold, subducted oceanic lithosphere, have been consistently observed at depths greater than 670 km using seismic tomography (e.g., Durand et al., 2017; Hosseini et al., 2020; Koelmeijer et al., 2016). At higher spatial resolutions, regional seismic studies corroborate dynamic studies in their observations of material with elevated seismic wave speeds throughout the deepest parts of the mantle (Schumacher & Thomas, 2016; Sun et al., 2019). Accurate and quantitative interpretations of seismic studies and inferences of lower mantle structure requires thorough knowledge of the effects of compositional variations on observed seismic velocities and impedance contrasts, constrained in part by the equations of state of relevant mineral phases and their solid solutions.

In the case of subducted slabs, relevant compositions may include hydrous components formed in oceanic lithosphere and carried to greater depth. For example, phase “Egg” (AlSiO(OH)) has been observed as nanocrystalline inclusions in diamonds recovered from the mantle transition zone (Wirth et al., 2007). The discovery of ice-VII (Tschauener et al., 2018) and hydrous ringwoodite (Pearson et al., 2014) as inclusions in diamonds exhumed from the transition zone also suggests the presence of aqueous fluid in this region. While dense hydrous magnesium silicate phases are expected to dehydrate along typical geotherms in the upper mantle or transition zone (Boffan-Casanova, 2005), recently synthesized hydrous phases such as δ-AlOOH (“delta phase”), MgSiO(OH)2 (“phase H”) and ε-FeOOH have been observed to be stable at temperatures and pressures relevant to the lowermost mantle and form from the components of hydrous metabasalts (X. Liu et al., 2019). In particular, δ-AlOOH has garnered interest as a candidate carrier of hydrogen to the deep mantle (Ohtani, 2020; Ohtani et al., 2018) due to its stability at temperatures potentially as high as those of the ambient mantle near the core-mantle boundary (Sano et al., 2008; Terasaki et al., 2012). However, recent synthesis experiments have revealed δ-AlOOH to be an endmember component of the (δ-AlOOH)-(MgSiO(OH)2)-(ε-FeOOH) solid solution (Komatsu et al., 2011; X. Liu et al., 2019; Ohira et al., 2014). Therefore, studying the effect of compositional variation in this system will be necessary to understand the seismic signature of subducted lithosphere and distinguish between different hypotheses concerning the origin of seismic reflectors and structure within the lower mantle (e.g., Panero et al., 2020).

The aluminum oxy-hydroxide δ-AlOOH is a high-pressure polymorph of diaspore (α-AlOOH), first synthesized by Suzuki et al. (2000) at 21 GPa and 1273 K with small amounts of magnesium and silicon (δ-Al0.38Mg0.07Si0.63O(OH)). At ambiant conditions, δ-AlOOH and ε-FeOOH adopt the space group P21/nm with ordered and asymmetric hydrogen bonds (Gleason et al., 2013; Suzuki et al., 2000; Thompson et al., 2017). These two phases have been further observed to form a solid solution (Kawazoe et al., 2017; Nishi et al., 2017). Changes in hydrogen bonding environment due to compression have been observed in single crystal X-ray diffraction, neutron diffraction, and infrared spectroscopy measurements on δ-AlOOH (Kagi et al., 2010; Kuribayashi et al., 2014; Sano-Furukawa et al., 2018). The symmetrization of hydrogen bonds in ε-FeOOH has been inferred from changes in relative compressibilities along different crystallographic directions and prompts a change in space group from P21/nm to Pnma near 18 GPa (Thompson et al., 2020), a pressure lower than the symmetrization pressure predicted by density functional theory calculations performed for this composition by Gleason et al. (2013) (42 GPa) but similar to the calculations of Thompson et al. (2017) (17.5 GPa). Similar observations have been used to infer an order-disorder transition of hydrogen bonds in δ-(Al, Fe)OOH near 10 GPa (Ohira et al., 2019). Nuclear magnetic resonance measurements reported by Meier et al. (2022) corroborate the change in space group from P21/nm to Pnma observed at ~10 GPa in δ-(Al, Fe)OOH and conclude that hydrogen bond symmetrization occurs at a pressure of approximately 22 GPa.

MgSiO(OH)2 (phase H) crystallizes in the space group Pnma with disordered hydrogen bonds (Bindi et al., 2014). X-ray diffraction measurements at high pressure revealed changes in relative compressibilities along different crystallographic axes near 30 GPa, indicating that hydrogen bonds in MgSiO(OH)2 may become symmetric at this pressure (Nishi et al., 2018). The solid solution between δ-phase and phase H was confirmed to coexist with alumina-depleted bridgmanite in the lower mantle (Ishii et al., 2022; Ohira et al., 2014). X. Liu et al. (2019) observed the formation of a solid solution between δ-AlOOH, MgSiO(OH)2, and ε-FeOOH (referred to as “Al-rich phase H”) coexisting with calcium silicate perovskite (or davemaoite, Tschauener et al., 2021), stishovite, magnesiowüstite, and fluid at 25–26.3 GPa and 1273–1473 K from compression and heating of a natural, hydrous basalt. However, the compressional behavior of an intermediate composition in the (δ-AlOOH)-(MgSiO(OH)2)-(ε-FeOOH) solid solution at pressures throughout the lowermost mantle has not yet been described.
The compressibility of this solid solution may be affected by changes in hydrogen bonding environment as well as a spin transition of ferric iron (Fe$^{3+}$) at high pressure. The formation of short, strong hydrogen bonds by disordering and eventually of symmetric hydrogen bonds is likely important in preventing the dissociation of these hydrous phases at the high temperatures of the lower mantle. A spin transition will affect the elastic properties of Fe-bearing compositions in this solid solution at lower mantle depths. The decreases in bulk modulus across the range of pressures corresponding to a spin crossover have been previously observed in studies of (Mg, Fe)O (Chen et al., 2012; Lin & Tsuchiya, 2008; Solomatova et al., 2016), Fe$^{3+}$-bearing bridgmanite (Dorffman et al., 2015; Mao et al., 2015), and other Fe-bearing minerals (e.g., J. Liu et al., 2015; Wu et al., 2016). The pressure range of the spin crossover and its effects on compressibility are governed in part by the valence state(s) of the iron atom(s), their coordination environment, and the electric field gradient imposed by the surrounding anions, whose pressure dependence is related to how strain is accommodated within the crystal structure. At quasi-hydrostatic conditions, changes in compressibility reflected in the equation of state of a material should precisely measure the breadth of a Fe$^{3+}$ spin crossover, though the inferred pressures of this crossover may vary by several percent between studies based on the pressure calibration used (see Section 3.2). Additionally, techniques which are directly sensitive to the electronic and magnetic states of Fe atoms (e.g., synchrotron Mössbauer spectroscopy [SMS] or X-ray emission spectroscopy) can be more sensitive to low proportions of low-spin Fe and may discern broader pressure intervals of the spin crossover. Ohira et al. (2019) inferred a high-low spin transition of Fe$^{3+}$ in δ-(Al,Fe)OOH with two different iron concentrations (Fe/(Al + Fe) = 0.047(10) (δ-Fe5) and Fe/(Al + Fe) = 0.123(2) (δ-Fe12)) near 35 GPa based on synchrotron powder X-ray diffraction measurements and confirmed a change in spin state of the Fe$^{3+}$ atoms by SMS on a similar composition with Fe/(Al + Fe) = 0.13(2). Additionally, Nishi et al. (2019) observed a volume collapse due to the Fe$^{3+}$ spin crossover in δ-(Al,Fe)OOH with Fe/(Al + Fe) = 0.21 (δ-Fe21) and Fe/(Al + Fe) = 0.64 (δ-Fe6) at ~45 GPa using X-ray diffraction. In the (δ-AlOOH)-(MgSiO$_3$)(OH)$_2$-(e-FeOOH) solid-solution, the incorporation of Mg and Si could affect the way in which strain is accommodated by Fe-O bonds and therefore result in important differences in the spin transition characteristics and compressional behavior in comparison to δ-(Al,Fe)OOH. Here, we use synchrotron powder X-ray diffraction to determine the equation of state, including the effects of hydrogen bond symmetrization and the high-low spin transition of iron, of Al$_{0.34}$Fe$_{0.66}$Si$_{0.02}$O$_{2.07}$OH (hereafter referred to as “(Al,Fe)-phase H”) to 125 GPa. SMS is used to constrain the hyperfine parameters of Fe$^{3+}$ in (Al,Fe)-phase H and to monitor the change in spin state. Additional SMS measurements are performed on δ-(Al,Fe)OOH with Fe/(Al + Fe) = 0.123(3) (δ-Fe13) to understand the effect of composition on changes in spin state. The collective results are discussed in the context of important transitions in these phases and their implications for the signature of subducted, hydrous lithosphere in the lower mantle.

2. Methods

2.1. Synthesis of (Al, Fe)-Phase H Crystals

(Al, Fe)-phase H crystals were synthesized with a hydrothermal method using a 1,000-ton Kawai-type multi-anvil apparatus installed at the Bayerisches Geoinstitut, University of Bayreuth (BGI). The starting material was a mixture of 80% Al(OH)$_3$, 6% MgO, 6% SiO$_2$, and 8% Fe$_2$O$_3$ (96.64% enriched with $^{57}$Fe) by weight. The starting material was compressed to 21 GPa and heated to 1470 K at a rate of 40–50 K/min. This temperature was held constant for a total of 4 hr before rapid quenching. To determine the chemical composition and crystal structure of (Al, Fe)-phase H, a recovered single crystal with dimensions of about 50 × 50 × 50 μm was selected based on the absence of twinning observed by X-ray diffraction and sharp optical extinction when viewed between crossed polarizers with a polarizing microscope. The chemical composition of the recovered crystal was measured to be Al$_{0.34}$Fe$_{0.66}$Si$_{0.02}$O$_{2.07}$OH using an electron microprobe operating at 15 kV and 10 nA in wavelength-dispersive mode (JEOL, JXA-8200 installed at Tohoku University). Synthetic hematite and corundum were used as standard materials for Fe and Al, respectively. Natural enstatite was employed as a standard material for Mg and Si. The high-pressure experiments described below used grains from this synthesis which were cut into smaller pieces and crushed into a powder. δ-(Al, Fe)OOH crystals with Al/(Al + Fe) = 0.87 (hereafter referred to as “δ-Fe13”) used for synchrotron Mössbauer measurements were synthesized at 27 GPa and 1500 K for 5 hr using the 1,500-ton Kawai-type multi-anvil apparatus with Osugi-type guide block system installed at BGI (Ishii et al., 2019, 2016). A detailed description of the synthesis of these crystals is given in Buchen et al. (2021).
2.2. X-Ray Diffraction

Single crystal X-ray diffraction patterns of the recovered (Al, Fe)-phase H crystal were collected using a Huber Eulerian cradle single-crystal diffractometer with a Mo Kα X-ray source operated at 50 kV and 40 mA and a point detector. The diffractometer was controlled by the SINGLE software (Angel & Finger, 2011). Unit cell parameters of crystals with a half-width of the diffraction peaks less than 0.1° were refined using the vector least squares method (Ralph & Finger, 1982). The effect of crystal offsets and diffractometer aberrations for each crystal were eliminated using the eight-position centering method (King & Finger, 1979). X-ray diffraction measurements for structural refinement were made separately using an area detector. The WinGX program (Farrugia, 2012) was employed for space group assignment and structure refinement (see Section 3.1). The initial structure for the refinement was found using the direct method of the SHELXL-97 program (Sheldrick, 1997). Refinement of the structure was performed against IFI2 using the full-matrix least squares method with the scattering factors of neutral atoms from the International Tables for Crystallography (Wilson, 1992).

Powdered (Al, Fe)-phase H was loaded in a symmetric diamond anvil cell (DAC) for high-pressure X-ray diffraction measurements. Beveled Type IA diamonds with culet diameters of 250 μm were used as the anvils. A rhenium foil with initial thickness of about 250 μm was pre-indented to a thickness of 40 μm for use as the gasket. To form the sample chamber, a 70 μm diameter hole was drilled at the center of the gasket indentation using an electric discharge machine. Powdered (Al, Fe)-phase H was loaded into the sample chamber with a ruby sphere and gold powder to serve as pressure gauges. Compressed helium gas was loaded at 25,000 PSI at the California Institute of Technology to serve as a quasi-hydrostatic pressure-transmitting medium. At beamline 13-ID-D of GSECARs at the Advanced Photon Source at Argonne National Laboratory (Lemont, IL, USA), the DAC was connected to a membrane-driven pressure control system. Angle-dispersive X-ray diffraction patterns were collected on a Pilatus IM CdTe area detector using monochromatic X-rays (λ = 0.3344 Å) focused to a size of 2 μm (vertical) by 3 μm (horizontal) at the sample position. Calibration of the instrument resolution function, sample-detector distance, and detector tilt was performed by collecting a diffraction pattern of LaB6 powder in air, using the known X-ray wavelength and pixel area. Diffraction patterns of (Al, Fe)-phase H were collected at 159 pressures between 4.0 and 123 GPa. Patterns were collected with an exposure time of 10 s, during which the sample was rotated by 10° about its vertical axis.

Two-dimensional angle-dispersive X-ray diffraction patterns were integrated to one-dimensional profiles of diffracted intensities versus 2θ angle using the DIOPTAS software (Prescher & Prakapenka, 2015). Background subtraction was performed using the “sbck” module of the MINUTI software package (Sturhahn, 2022) which detects and removes background common to all diffraction profiles in a coherent stack of profiles. By iteratively searching the lowest intensity at specific 2θ angles in the stack of normalized diffraction profiles, sbck yields a refined background function which is subsequently removed from individual diffraction profiles. Inspection of the processed diffraction profiles after background subtraction ensures that sample reflections remain undistorted. An example of the results of the sbck background subtraction routine for a pattern collected at 7 GPa is shown in Figure 1a. Full-pattern Pawley refinement of each diffraction profile is performed using the GSAS-II software package (Toby & Von Dreele, 2013). An example fit to a pattern collected at 7 GPa is shown in Figure 1b. All reported pressures for the sample are determined using the refined unit cell volumes of gold and the equation of state given by Fei et al. (2007a).

2.3. Equation of State Fitting

The pressure-volume data of (Al, Fe)-phase H obtained from the powder X-ray diffraction measurements was fit to a spin crossover equation of state using the MINUTI software package (Sturhahn, 2022). The MINUTI software package implements an equation of state model which accounts for both the elastic and spin contributions (arising from the spin state of the 3d electrons of the Fe atoms) to the free energy of the sample. For a third order Birch-Murnaghan equation of state, the elastic component of the free energy is given by Equations 1 and 2:

\[ F_o(V) = \frac{9}{2} K_0 V_0 f^2 \left\{ 1 + f \left( K'_0 - 4 \right) \right\} \]  
\[ f = \frac{1}{2} \left\{ \left( \frac{V_0}{V} \right)^{2/3} - 1 \right\} \]

where \( F_o(V) \) is the free energy, \( V_0 \) is the unit cell volume at zero pressure, and \( K_0 \) and \( K'_0 \) are the isothermal bulk modulus and its pressure derivative, respectively.
where $K_0$ represents the bulk modulus at zero pressure, $K'_0$ refers to the gradient $dK/dP$ at zero pressure, $V_0$ is the unit cell volume at zero pressure, and $f$ is the Eulerian strain. The component of the free energy attributable to the spin state of the Fe atoms is given by Equation 3:

$$F_s(V, T) = -k_B T \ln(Z_s)$$

where $k_B$ is the Boltzmann constant, $T$ is the temperature, and $Z_s$ is the spin partition function, defined for the relevant atom (here Fe$^{3+}$) by the number of unpaired electrons, volume-dependent energy, and orbital degeneracy. When fit to experimental $P$-$V$ data, this model locates the region of the spin crossover and describes changes in density and compressibility resulting from the spin transition. Equations of state for the high and low-spin states are fit simultaneously. Additional details are given in the MINUTI manual (Sturhahn, 2022).

It is well known that estimates of uncertainties on refined unit cell parameters are typically underestimated by full-profile refinement protocols. Therefore, we follow the procedure recommended by Angel (2000)

Figure 1. (a) Example background subtraction using the MINUTI sbck module (nrixs.com). The collected diffraction profile has a substantial but smooth background which can be removed from each profile in the stack to produce a “background subtracted profile” that is more amenable to fitting using whole-profile refinement methods. (b) Example fit to the same background subtracted profile using the Pawley refinement procedure of the GSAS-II software (Toby & Von Dreele, 2013).
implemented in Morrison et al. (2018) in scaling the uncertainties (σ) on unit cell edge lengths by an empirical scaling factor k such that a fit to an appropriate equation of state model produces χ² ≈ 1. So long as the model used to fit the data is appropriate, χ² ≫ 1 indicates that the variance of the data has been underestimated while χ² ≪ 1 indicates an overestimate of the variance. Uncertainties on unit cell edge lengths for both the gold pressure calibrant and (Al, Fe)-phase H sample are scaled by a factor of k = 1.5. The scaled uncertainties were subsequently used to calculate the standard deviation of unit cell volumes using standard formulae to propagate experimental uncertainties. Uncertainties in pressure were estimated using the scaled uncertainties of the unit cell volumes of gold, neglecting any uncertainties on the equation of state parameters of gold (Fei et al., 2007a) since their covariance matrix is not reported.

2.4. Synchrotron Mössbauer Spectroscopy

Two symmetric DACs were loaded with powdered (Al, Fe)-phase H and two with δ-(Al, Fe)OOH with Fe/ (Al + Fe) = 0.13 (δ-Fe13) for SMS measurements conducted at beamline 3-ID-B of the Advanced Photon Source, Argonne National Laboratory. Each DAC was loaded with a small ruby sphere (~10 μm diameter) proximal to the center of the gasket hole for online pressure determination using the calibration of Dewaele et al. (2008). For measurements on (Al, Fe)-phase H, one DAC with 400 μm diameter culets was loaded with compressed He gas at the California Institute of Technology. The measured pressure after gas loading was 1.5 GPa and measurements were performed to a maximum pressure of 22 GPa. A second set of SMS measurements was performed using a DAC with beveled, 300 μm diameter culets at pressures from 0.03 to 53 GPa. For these experiments, the cell was shipped to the Advanced Photon Source and loaded with compressed He gas at the GSECARS/COMPRES gas loading system. Synchrotron Mössbauer spectra were collected on δ-Fe13 samples from 2 to 23 GPa and 15–47 GPa using DACs with 400 μm flat and 250 μm beveled culets, respectively and loaded with compressed He gas at the California Institute of Technology.

Time-domain SMS measurements were performed for the (Al, Fe)-phase H and δ-Fe13 experimental runs during which the storage ring was operated in top-up mode with 24 bunches separated by 153 ns. The beam was focused on an area of 16 × 16 μm² at the sample position using a Kirkpatrick-Baez mirror system. A high-resolution monochromator was tuned to the 14.4125 keV nuclear transition energy of ⁵⁷Fe (Toellner, 2000) and the resonance monitored during collection of time spectra to optimize counting rates. Additional measurements were collected in hybrid mode for (Al, Fe)-phase H at a pressure of 1.5 GPa and δ-Fe13 at 24 GPa, using a focal area of 10 × 10 μm². Isomer shifts were derived relative to a stainless steel (SS) reference foil with a natural abundance of ⁵⁷Fe placed downstream of the sample. Measurements to constrain the isomer shift were taken at the lowest pressure point in each (Al, Fe)-phase H experimental run as well as at 40 GPa. Each reference foil was measured at the APS using a radioactive source to have isomer shifts relative to α-iron metal of −0.100(3) mm/s and −0.094(3) mm/s for the 5 μm and 10 μm thick SS310 foils, respectively (Solomatova et al., 2017).

Synchrotron Mössbauer spectra were fit with version 2.2.2 of the CONUSS software (Sturhahn, 2000) using a time window between 25 and 120 ns in 24-bunch mode and from 50 to 250 ns in hybrid mode. The CONUSS software implements a least squares algorithm to refine the hyperfine parameters of iron and the effective thickness of the sample. The effective thickness is dimensionless and is the product of the numerical density of the ⁵⁷Fe atoms, the physical thickness of the sample, the nuclear resonant cross-section (2.56 × 10⁻²² m² for ⁵⁷Fe), and the Lamb-Mössbauer factor (fraction of recoil-free scattering events). For compression points at which a spectrum was collected with the stainless reference foil, a simultaneous fit of both spectra (with and without the reference foil) was performed. Starting models were informed by the hyperfine parameters of δ-(Al, Fe)OOH reported in Ohira et al. (2019). In fitting SMS spectra of δ-Fe13 in this study, the Lamb-Mössbauer factor at each pressure is interpolated from the Lamb-Mössbauer factors reported in Ohira et al. (2021). The same interpolation is applied to estimate the Lamb-Mössbauer factor of (Al, Fe)-phase H at high pressure, disregarding the transition associated with hydrogen bond disorder in Ohira et al. (2021) as hydrogen bonds are likely disordered at ambient pressure in (Al, Fe)-phase H (see Results and Discussion).

3. Results

3.1. Crystal Structure of (Al, Fe)-Phase H

Single crystal X-ray diffraction patterns of (Al, Fe)-phase H (Al₀.⁶₅Fe₀.₃₅Mg₀.₀₇Mg₀₂Si₀.₀³)OHOH were indexed with the Pnma space group and yielded unit cell parameters at ambient pressure of a₀ = 4.7187(1) Å, b₀ = 4.2285(1) Å, c₀ = 2.8448(1) Å, and V₀ = 56.762(3) Å³. A rendering of the crystal structure is shown in Figure 2 and
a Crystallographic Information File (CIF) file provided in Supporting Information S1. The crystal structure constrained here is similar to that determined for Al-bearing phase H along the δ-AlOOH-MgSiO$_3$(OH)$_2$ join: Mg$_{0.50}$Si$_{0.44}$Al$_{0.055}$ (Bindi et al., 2015), with $a_0 = 4.730(2)$ Å, $b_0 = 4.324(2)$ Å, $c_0 = 2.843(1)$ Å, and $V_0 = 58.15(5)$ Å$^3$. (Al, Fe)-phase H crystallizes in the same CaCl$_2$-type structure with edge-sharing octahedra and hydrogen bonds that locate in the $a$-$b$ plane, albeit with different atomic positions. The substitution of small amounts of Fe$^{3+}$ for Al$^{3+}$ and higher concentration of Al relative to Mg and Si in (Al, Fe)-phase H may be responsible for the observed differences in unit cell edge lengths but does not result in a structural change. In both compositions, cations occupy a single octahedral site and hydrogen bonds are disordered at ambient pressure, as in the end-member MgSiO$_3$(OH)$_2$ composition (Bindi et al., 2014). The structure reported here agrees with the observation that a change in space group of δ-AlOOH from $P2_1$ to $Pnmm$ is provoked by substitution of even small amounts of Mg and Si for Al (Komatsu et al., 2011). In contrast, the replacement of Al$^{3+}$ by Fe$^{3+}$ substitution does not appear to cause a structural change (Kawazoe et al., 2017; Suzuki et al., 2000).

3.2. Powder X-Ray Diffraction and Equation of State

A reasonable estimate of the error in pressure when comparing the X-ray diffraction results presented here with previous measurements in the δ-AlOOH-(MgSiO$_3$(OH)$_2$)-(FeOOH) solid solution is <2%. Pressures reported in Duan et al. (2018) and Gleason et al. (2013) are calibrated with the equation of state of gold reported in Fei et al. (2007a). Thompson et al. (2020) use the Fei et al. (2007a) equation of state for neon. Pressures reported in those studies should therefore be consistent with those reported here. Ohira et al. (2019) used the calibration of the tungsten pressure scale by Dorogokupets and Oganov (2006), which records pressures that are systematically ∼1.7% greater than those of the Fei et al. (2007a) and gold calibration. The Tsuchiya (2003) Au equation of state used to determine pressure in the measurements of Nishi et al. (2019) reports pressures at the relevant pressures and 300 K that are approximately 3% higher than those reported in this study.

Figure 3 shows the normalized unit cell edge lengths and axial ratios of (Al, Fe)-phase H (Al$_{0.84}$Fe$_{0.16}$) compared to other compositions in the δ-AlOOH-(MgSiO$_3$(OH)$_2$)-(FeOOH) solid solution at 300 K (Duan et al., 2018; Gleason et al., 2013; Nishi et al., 2018; Ohira et al., 2019; Thompson et al., 2020). A comparison of normalized unit cell volumes of the same compositions is shown in Figure S1 in Supporting Information S1. The linear compressibility of the $a$-axis is the least sensitive to cation substitution at low pressure (Fe-bearing materials in the high-spin state), as indicated by the similarity in values of $a/a_0$ between different

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<th>$a_0$ (Å)</th>
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Figure 2. Crystal structure of (Al, Fe$^{3+}$)-phase H (Al$_{0.84}$Fe$_{0.16}$) (space group $Pnmm$) as determined by single crystal X-ray diffraction. The crystal structure is projected along the crystallographic $c$-axis. Octahedrally coordinated cations are represented by their colors in proportion to their concentration. A Crystallographic Information File (CIF) containing atomic coordinates and structure parameters is available as a supporting file. This figure was created with VESTA (Momma & Izumi, 2011).
The subtle kinks in the compression trends of $a/a_0$, $b/b_0$, and $c/c_0$ in (Al, Fe)-phase H near 55 GPa are the result of a volume collapse due to a spin transition. There is comparatively little variance in $a/a_0$ or $c/c_0$ due to composition in the pressure range shown relative to that observed for $b/b_0$. The crystal structure of $\delta$-AlOOH appears to be most sensitive along the $b$-axis to the incorporation of Fe$^{3+}$: $\delta$-Fe5 exhibits lower values of $b/b_0$.

Figure 3. Normalized unit cell edge lengths and axial ratios for compositions in the ($\delta$-AlOOH)-(MgSiO$_2$(OH)$_2$)-($\epsilon$-FeOOH) solid solution at 300 K. Measurements at high pressure are obtained from Ohira et al. (2019): $\delta$-Al$_{0.95}$Fe$_{0.05}$OOH ($\delta$-Fe5) and $\delta$-Al$_{0.88}$Fe$_{0.12}$OOH ($\delta$-Fe12), Nishi et al. (2018): MgSiO$_2$(OH)$_2$, Duan et al. (2018): $\delta$-AlOOH, and the combined data sets of Gleason et al. (2013), Nishi et al. (2019), and Thompson et al. (2020): $\epsilon$-FeOOH. Unit cell edge lengths at high pressure are normalized by their values at ambient pressure determined by single crystal X-ray diffraction measurements on the same composition: this study (Al, Fe)-phase H, Kawazoe et al. (2017): ($\delta$-Fe5 and $\delta$-Fe12), Bindi et al. (2014): MgSiO$_2$(OH)$_2$, Kuribayashi et al. (2014): $\delta$-AlOOH, and Suzuki (2010): $\epsilon$-FeOOH. Values of $a/c$ for $\delta$-Al$_{0.79}$Fe$_{0.21}$OOH ($\delta$-Fe21), $\delta$-Al$_{0.36}$Fe$_{0.64}$OOH ($\delta$-Fe64), and Mg$_{0.17}$Si$_{0.17}$Al$_{0.33}$Fe$_{0.63}$OOH reported by Nishi et al. (2019) are shown in the lower right panel of this figure.
relative to $\delta$-AIOOH and $\delta$-Fe12 has even lower values. However, this effect does not remain with the substitution of Mg and Si as the length of the crystallographic $b$-axis in (Al, Fe)-phase $\text{H}$ appears to be more invariable to pressure. Ohira et al. (2019) inferred the symmetrization of hydrogen bonds in $\delta$-(Al, Fe)OOH with Fe/(Al + Fe) = 0.12 ($\delta$-Fe12) and Fe/(Al + Fe) = 0.05 ($\delta$-Fe5) at approximately 10 GPa based on changes in the trend of the axial ratios as well as on a change in space group from $P2_{1}nm$ to $Pmmm$. To pressures of about 30 GPa, the trends in ratios of unit cell edge lengths versus pressure observed in (Al, Fe)-phase $\text{H}$ are flat, especially when compared to the same trends observed in $\delta$-(Al, Fe)OOH (Figure 3). At pressures greater than 30 GPa, the decrease in the ratio $a/b$ with pressure is steeper than what is observed for $\delta$-(Al, Fe)OOH, regardless of iron concentration. The ratio $a/c$ remains approximately constant to a pressure of 120 GPa whereas the magnitude of the increase of $b/c$ with pressure is similar to that observed in $\delta$-(Al, Fe)OOH. The ratio $a/c$ of (Al, Fe)-phase $\text{H}$ is lower than for $\delta$-(Al, Fe)OOH and is the lowest for Mg$_{0.17}$Si$_{0.17}$Al$_{0.63}$OOH, implying that increasing concentration of Mg and Si in $\delta$-(Al, Fe)OOH decreases $a/c$. Axial ratios of $\delta$-AIOOH (Duan et al., 2018) exhibit the same general trends observed for $\delta$-(Al, Fe)OOH to 120 GPa.

Figure 4 shows $P-V$ data for compositions in the $\delta$-(AIOOH)-(MgSiO$_{2}$)(OH)$_{2}$-($\epsilon$-FeOOH) solid solution and the equation of state constrained for (Al, Fe)-phase $\text{H}$. For clarity, the much larger unit cell volumes of $\epsilon$-FeOOH are not plotted. Comparison of $\epsilon$-FeOOH to other compositions based on normalized unit cell volumes is shown in Figure S1 in Supporting Information S1. Equation of state parameters for compositions plotted in Figure 4 are given in Table 1. In Table 1, the data range for a spin equation of state includes all data used in the fit, with the spin transition pressure and width as free parameters. The spin transition pressure determined by fitting the spin crossover equation of state is defined as the pressure at which the change in unit cell volume due to the spin transition is 50% complete, constrained here for (Al, Fe)-phase $\text{H}$ as 55.5 ± 0.9 GPa. The spin crossover region determined from the equation of state is 48–63 GPa (width of 15 GPa at 300K). This region does not overlap with the spin crossover determined for $\delta$-(Al, Fe)OOH. On the basis of changes in the unit cell volume, the spin crossover in $\delta$-(Al, Fe)OOH occurs over a pressure range of approximately 8 GPa and is 50% complete in $\delta$-Fe5 at 35(1) GPa, and 36.1(7) GPa, in $\delta$-Fe12 (Ohira et al., 2019). Figure 5 illustrates correlations between

![Figure 4. $P-V$ data for (Al, Fe)-phase $\text{H}$ fit to a spin equation of state using the MINUTI software package ($\chi^2 = 1.21(9)$). For discussion of uncertainties in fitting $P-V$ data to an equation of state see the methods section. The gray shaded region indicates the spin crossover region (total width ~ 15 GPa) determined by fitting the spin equation of state. The equation of state is compared to unit cell volume data for other compositions in the $(\delta$-AIOOH)-(MgSiO$_{2}$)(OH)$_{2}$-($\epsilon$-FeOOH) solid solution at 300 K. $P-V$ data for other compositions were obtained from Ohira et al. (2019): $\delta$-Fe5 and $\delta$-Fe12, Nishi et al. (2018): MgSiO$_{2}$(OH)$_{2}$, Duan et al. (2018): $\delta$-AIOOH, and Nishi et al. (2019): $\delta$-Fe21 and $\delta$-Fe64. Due to the significantly larger unit cell volume, data for $\epsilon$-FeOOH is omitted from this figure for clarity.](image)

### Table 1

<table>
<thead>
<tr>
<th>Composition</th>
<th>EOS type</th>
<th>Data range (GPa)</th>
<th>$V_0$ (Å$^3$)</th>
<th>$K_{0\text{H}}$ (GPa)</th>
<th>$K_{0\text{H}}^{\text{m}}$ (GPa)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al$<em>{0.44}$Fe$</em>{0.56}$Mg$<em>{0.02}$Si$</em>{0.96}$O(OH)</td>
<td>Spin EOS (HS)</td>
<td>0–125</td>
<td>56.76(1)</td>
<td>161(1)</td>
<td>6.2(1)</td>
<td>This study</td>
</tr>
<tr>
<td>Al$<em>{0.34}$Fe$</em>{0.66}$Mg$<em>{0.02}$Si$</em>{0.96}$O(OH)</td>
<td>Spin EOS (LS)</td>
<td></td>
<td>54.3(5)</td>
<td>227(24)</td>
<td>5.5(4)</td>
<td></td>
</tr>
<tr>
<td>$\delta$-(Al$<em>{0.1985}$Fe$</em>{0.0015}$)(OH)$_{2.143}$</td>
<td>Spin EOS (HS)</td>
<td>12.4–55.6</td>
<td>56.9(4)</td>
<td>149(25)</td>
<td>8(2)</td>
<td>Ohira et al. (2019)</td>
</tr>
<tr>
<td>$\delta$-(Al$<em>{0.9005}$Fe$</em>{0.0455}$)(OH)$_{2.143}$</td>
<td>Spin EOS (LS)</td>
<td></td>
<td>55.4</td>
<td>223(11)</td>
<td>4(4 fixed)</td>
<td></td>
</tr>
<tr>
<td>$\delta$-(Al$<em>{0.1800}$Fe$</em>{0.1730}$)(OH)$_{2.153}$</td>
<td>Spin EOS (HS)</td>
<td>10.1–64.8</td>
<td>57.5(3)</td>
<td>155(22)</td>
<td>8(2)</td>
<td>Ohira et al. (2019)</td>
</tr>
<tr>
<td>$\delta$-(Al$<em>{0.1800}$Fe$</em>{0.1730}$)(OH)$_{2.153}$</td>
<td>Spin EOS (LS)</td>
<td></td>
<td>55.2(4)</td>
<td>241(14)</td>
<td>4(4 fixed)</td>
<td></td>
</tr>
<tr>
<td>$\delta$-AIOOH</td>
<td>3 BM</td>
<td>20–130</td>
<td>55.32(2 fixed)</td>
<td>223(3)</td>
<td>4.0(2)</td>
<td>Duan et al. (2018)</td>
</tr>
<tr>
<td>$\epsilon$-FeOOH</td>
<td>3 BM (LS)</td>
<td>DFT</td>
<td>58.62(3)</td>
<td>223(4)</td>
<td>4.07(2)</td>
<td>Thompson et al. (2017)</td>
</tr>
<tr>
<td>MgSiO$<em>{2}$(OH)$</em>{2}$</td>
<td>2 BM</td>
<td>33.8–60.2</td>
<td>56.6(1)</td>
<td>204(2)</td>
<td>4(4 fixed)</td>
<td>Nishi et al. (2018)</td>
</tr>
</tbody>
</table>

Note. “HS” refers to the portion of the spin crossover equation of state which describes the high-spin state and “LS” refers to the portion which describes the low-spin state. “2 BM” refers to a second order Birch-Murnaghan equation of state and “3 BM” refers to a third order Birch-Murnaghan equation of state. The spin equation of state is based on a third order Birch-Murnaghan equation of state (see methods). The equation of state used for $\epsilon$-FeOOH is generated by density functional theory (DFT) calculations described in the associated reference.
unit cell volume and the isothermal bulk modulus of \( \delta \)-(Al, Fe)OOH and (Al, Fe)-phase H at various pressures as confidence ellipses obtained from the equation of state fits, further discussed below.

### 3.3. Synchrotron Mössbauer Spectroscopy

Fits to (Al, Fe)-phase H (Al\(_{0.84}\)Fe\(_{0.07}\)Mg\(_{0.02}\)Si\(_{0.06}\)OOH) SMS spectra collected in 24-bunch mode are shown in Figure 6. Fits to spectra collected on \( \delta \)-(Al, Fe)OOH with Fe/(Al + Fe) = 0.13 (\( \delta \)-Fe13) in 24-bunch mode are shown in Figure S2 in Supporting Information S1. Hyperfine parameters determined for each phase are given in Tables 2–3 ((Al, Fe)-phase H) and Tables S1–S2 in Supporting Information S1 (\( \delta \)-Fe13). Mössbauer spectra collected in 24 bunch mode (delay times of 25–150 ns) at low pressures (\( P < 33 \) GPa) during both (Al, Fe)-phase H experimental runs are well described using a model with a single ferric iron site (Fe\(_{\text{A}}^{3+}\)), in accordance with the single crystallographic site occupied by Fe\(_{\text{A}}^{3+}\) in the crystal structure of (Al, Fe)-phase H. The best-fitting model at pressures higher than 33 GPa requires the introduction of a second site (Fe\(_{\text{B}}^{3+}\)) that is distinguishable from Fe\(_{\text{A}}^{3+}\) by its hyperfine parameters. The spectra collected on \( \delta \)-Fe13 also require the introduction of a second site at \( \sim 40 \) GPa. When multiple sites are required to fit the Mössbauer spectra, we perform a Monte Carlo search over a large parameter space using the CONUSS module kmco. Good models at each pressure cannot be obtained by fixing the weight fractions of the Mössbauer sites over a pressure range as performed in Ohira et al. (2019). Instead, the weight fractions of the two sites at each pressure are obtained by the best sampling in the monte carlo parameter search. Least squares refinement of hyperfine parameters, physical thickness, and sample texture are then performed using the CONUSS module “kctl” to determine the best model.

Hybrid mode collection allows access to longer delay times than data collected in 24-bunch mode, as shown in Figure S3 in Supporting Information S1. Access to longer delay times provides improved spectral resolution and
Resultant hyperfine parameters, uncertainties in pressure, and fits for data collected in 24-bunch mode and without a reference foil are shown at each measured pressure. Spectra are arbitrarily offset for clarity. Fits to time-domain spectra using the CONUSS software package are performed to time-domain spectra using the CONUSS software package.

**Figure 6.** Synchrotron Mössbauer spectroscopy spectra of (Al, Fe)-phase H and fits for data collected in 24-bunch mode and without a reference foil are shown at each measured pressure. Spectra are arbitrarily offset for clarity. Fits to time-domain spectra using the CONUSS software package. Resultant hyperfine parameters, uncertainties in pressure, and $\chi^2$ values are given in Tables 2 and 3.

allows for more precise fitting of potentially minor Fe sites or small differences in model parameters, including differences which may arise from deviatoric stresses. In contrast to the data collected in 24-bunch mode, the hybrid mode spectra for both (Al, Fe)-phase H (1.50 GPa) and $\delta$-Fe13 (23.31 GPa) require a second site to obtain the best model (Table 3 and Table S2 in Supporting Information S1). At 1.5 GPa in (Al, Fe)-phase H, the two sites have approximately equal weight with distinct hyperfine parameters. Site A has an isomer shift, quadrupole splitting, and full width at half-maximum (FWHM) values of 0.308(3), 0.494(3), and 0.236(1) in units of mm/s. These values are similar to those used in the single site model of the spectrum collected during 24-bunch mode at this pressure. In contrast, site B is broad (FWHM = 1.31(1) mm/s) and has a higher isomer shift (0.574(9) mm/s) and lower quadrupole splitting (0.29(2) mm/s). At 23.31 GPa in $\delta$-Fe13, the hyperfine parameters of the two sites differ only slightly (Table S1 in Supporting Information S1). Site A is the dominant contributor to the observed spectrum (wt. fraction = 0.9). A comparison of the two-site model to the best models obtained using a single site is shown in Figure S3 in Supporting Information S1.

The quadrupole splittings determined from 24-bunch mode data in this study are compared to those determined for $\delta$-(Al, Fe)OOH (Ohira et al., 2019) in Figure 7a. Comparison of isomer shifts and weight fractions of the Mössbauer sites are plotted in Figures 7b and 7c, respectively. At low pressure, low values of quadrupole splitting and isomer shift confirm the sole presence of ferric iron (Fe$^{3+}$) (Bromley & Hilairet, 2005; De Grave et al., 2006; Douvalis et al., 2000; Dyar et al., 2006; Lyubutin et al., 2009) in both (Al, Fe)-phase H and $\delta$-(Al, Fe)OOH. Quadrupole splittings of the A site in (Al, Fe)-phase H exhibit a general decrease with pressure from a value of 0.403(2) to 0.177(2) mm/s at 32.13 GPa. Quadrupole splittings of the A site in $\delta$-Fe13 are approximately constant across the same pressure range. Between 34 and 45 GPa, quadrupole splittings of both Fe$^{3+}_A$ and Fe$^{3+}_B$ increase for both compositions. Over the same pressure range, the weight fraction of the Fe$^{3+}_A$ site (lower quadrupole splitting) in (Al, Fe)-phase H decreases, achieving a minimum value of 0.34 in (Al, Fe)-phase H at 40.1 GPa. The quadrupole splitting of the Fe$^{3+}_A$ site in (Al, Fe)-phase H increases disproportionately at pressures higher than 45 GPa relative to that of the Fe$^{3+}_B$ site, which plateaus and then increases gradually. In contrast, the quadrupole splittings of each site in $\delta$-Fe13 increase relatively smoothly and approach the values determined at higher pressures in Ohira et al. (2019).

Values of the isomer shift decrease with increasing pressure for both (Al, Fe)-phase H and $\delta$-(Al, Fe)OOH (Figure 7b), reflecting an increase in s-electron density at the nucleus of the Fe atom due to compression. At $\sim$40 GPa in (Al, Fe)-phase H, the best-fitting model has two sites with identical isomer shifts relative to $\alpha$-Fe (0.145(6) mm/s), which does not unambiguously determine the spin state of the Fe atoms. In contrast, the fits to $\delta$-(Al, Fe)OOH spectra above 37 GPa require low or negative isomer shifts for site A (Table S2 in Supporting Information S1) that identify low-spin Fe$^{3+}$ (Gütlich and Garcia, 2012). Isomer shifts constrained on the same composition in Ohira et al. (2019) are significantly higher but still reflect values typical of low-spin Fe$^{3+}$.

### 4. Discussion

#### 4.1. Comparison to Previous Studies

A previous study of $\delta$-(Al$_{0.86}$Mg$_{0.07}$Si$_{0.07}$)OOH (Komatsu et al., 2011), revealed that substitution of even small amounts of Mg and Si into the structure of $\delta$-AlOOH results in disordering of hydrogen bonds at ambient pressure and in a change in space group from $P2_1/nm$ to $Pnm$. In contrast, substitution of ferric iron...
Table 2

Hyperfine Parameters of $^{57}$Fe$^{3+}$ in (Al, Fe)-Phase H (One Mössbauer Site)

<table>
<thead>
<tr>
<th>Pressure (GPa)</th>
<th>$W_T$</th>
<th>$I_{S_A}$ (mm/s)</th>
<th>$QS_A$ (mm/s)</th>
<th>$FWHM_A$</th>
<th>Thickness (μm)</th>
<th>Reduced $\chi^2$</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
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<td>0.03</td>
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<td>0.434(2)</td>
<td>0.139(5)</td>
<td>36.6(3)</td>
<td>1.9(1)</td>
<td>SS310 (5 μm)</td>
</tr>
<tr>
<td>1.5(2)</td>
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<td>-</td>
<td>0.541(1)</td>
<td>0.284(3)</td>
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<td>2.5(1)</td>
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</tr>
<tr>
<td>1.5(2)</td>
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<td>0.48(6)</td>
<td>0.472(3)</td>
<td>0.096(9)</td>
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<td>4.3(1)</td>
<td>SS310 (5 μm)</td>
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<tr>
<td>4.6(2)</td>
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<td>2.6(1)</td>
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</tbody>
</table>

Note. Hyperfine parameters and full-widths at half maximum (FWHM) of the measured spectra determined by fitting Synchrotron Mössbauer spectroscopy spectra collected in 24-bunch mode using a model with a single Fe$^{3+}$ site (QS, quadrupole splitting, IS, isomer shift). Isomer shifts are reported relative to $\alpha$-Fe based on the measured isomer shift of the stainless steel reference foil used (see methods). For measurements which use a reference foil, the reported $\chi^2$ indicates the value for a fit to both the reference and data.

Table 3

Hyperfine Parameters of $^{57}$Fe$^{3+}$ in (Al, Fe)-Phase H (Two Mössbauer Sites)

<table>
<thead>
<tr>
<th>Pressure (GPa)</th>
<th>$WT_A$</th>
<th>$I_{S_A}$ (mm/s)</th>
<th>$QS_A$ (mm/s)</th>
<th>$FWHM_A$</th>
<th>$WT_B$</th>
<th>$I_{S_B}$ (mm/s)</th>
<th>$QS_B$ (mm/s)</th>
<th>$FWHM_B$</th>
<th>Thickness (μm)</th>
<th>Reduced $\chi^2$</th>
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<tr>
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<td>0.318(3)</td>
<td>0.494(3)</td>
<td>0.236(1)</td>
<td>0.53</td>
<td>0.574(9)</td>
<td>0.29(2)</td>
<td>1.31(1)</td>
<td>28.7(6)</td>
<td>4.0(1)</td>
<td>SS310 (5 μm)</td>
</tr>
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<td>0.421(3)</td>
<td>0.106(8)</td>
<td>0.18</td>
<td>-</td>
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<td>-</td>
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<td>26.9(3)</td>
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Note. Hyperfine parameters of $^{57}$Fe$^{3+}$ in (Al, Fe)-phase H and full-widths at half maximum (FWHM) of the measured spectra determined by fitting Synchrotron Mössbauer spectroscopy spectra collected in 24-bunch mode using the CONUSS kctl module and a model with two Fe$^{3+}$ sites. Isomer shifts are reported relative to $\alpha$-Fe based on the measured isomer shift of the stainless steel reference foil used (see methods). For measurements with a reference foil, the reported $\chi^2$ indicates the value for a fit to both the reference and data. Hybrid mode measurements are denoted by a *.
for aluminum does not result in hydrogen bond disorder or a change in space group (Kawazoe et al., 2017). Therefore, the disordering of hydrogen bonds at ambient pressure in (Al, Fe)-phase H is likely due to the incorporation of Mg and Si as confirmed by our crystal structure determination (Figure 2, space group Pnmm), and the lack of an order-disorder transition upon compression, as observed for δ-(Al, Fe)OOH (Ohira et al., 2019).

The compressional behavior of (Al, Fe)-phase H (Al0.86Fe0.14)Mg0.96Si0.04(OH)2 δ-(Al, Fe)OOH is distinct from that of δ-(Al, Fe)OOH as well as that of the end-members δ-AI(OOH), MgSiO3(OH)2, and ε-FeOOH, implying the incorporation of Mg and Si into the crystal structure has important effects on bulk elastic properties relative to compositions which contain only Al and Fe. At pressures lower than 10 GPa, the bulk modulus of (Al, Fe)-phase H is comparable to that of δ-(Al, Fe)OOH (Figure 5) and the presence of Mg and Si in (Al, Fe)-phase H does not appear to exert a strong influence. Due to the order-disorder transition of hydrogen bonds, δ-(Al, Fe)OOH becomes less compressible than (Al, Fe)-phase H between 10 and 32 GPa (Figure 5). At 32 GPa, the high to low spin crossover of Fe3+ in δ-(Al, Fe)OOH results in increased compressibility compared to (Al, Fe)-phase H. At pressures greater than 70 GPa – where Fe3+ in both (Al, Fe)-phase H and δ-(Al, Fe)OOH is in the low-spin state—the bulk moduli and unit cell volumes of the two compositions remain clearly distinguishable, based on the correlations of these parameters from the respective equation of state models (Figure 5). Some of the differences in the constrained isothermal bulk moduli of δ-(Al, Fe)OOH and (Al, Fe)-phase H at pressures greater than 70 GPa may be due to the extrapolation of the equation of state determined in Ohira et al. (2019) from data collected at lower pressure. Ohira et al. (2019) fixed \( K'_V \) to a value of 4 in fitting data to the low-spin state of δ-(Al, Fe)OOH due to a lack of data above 70 GPa. This also marks the pressure at which the density, bulk modulus, and bulk sound velocity of (Al, Fe)-phase H begins to deviate from δ-(Al, Fe)OOH due to a considerably higher value of \( K'_V \) (Table 1). The larger isothermal bulk modulus of (Al, Fe)-phase H relative to δ-AI(OOH), δ-(Al, Fe)OOH, and ε-FeOOH may also be attributable to the substitution of Mg and Si into the crystal structure. The mechanism by which this substitution results in a less compressible crystal lattice is presently unclear but could be related to the specific way in which strain is accommodated within each crystal lattice, for which single crystal X-ray diffraction data is needed. With Mg2+ having the largest ionic radius of all cations in the δ-(AI(OOH)-(MgSiO3(OH)2)-(ε-FeOOH) solid solution, the large Mg cations might support the crystal structure and, to some extent, prevent the sites hosting smaller cations from contracting. The relative controls that cation substitution and the high-low spin crossover of Fe3+ place on the compressibility of the δ-(AI(OOH)-(MgSiO3(OH)2)-(ε-FeOOH) solid solution could be clarified by additional constraints on the equation of state of δ-(Al, Fe)OOH to pressures exceeding 70 GPa or an equation of state of another composition in this solid solution.
The onset of the spin transition at a lower pressure in δ-(Al, Fe)OOH (32–40 GPa) compared to ε-FeOOH led Ohira et al. (2019) to infer that the spin transition pressure in the (δ-AlOOH)-(ε-FeOOH) solid solution would increase with increasing iron concentration, an effect confirmed via Raman spectroscopy (Su et al., 2021a; Su et al., 2021b) and also observed for varying concentrations of Fe3+ in (Mg, Fe)O (Fei et al., 2007b; Lin et al., 2005; Solomatova et al., 2016). Nishi et al. (2019) observed a spin crossover of Fe3+ at approximately 46 GPa in δ-(Al, Fe)OOH with Fe/(Al + Fe) = 0.23 and Fe/(Al + Fe) = 0.67. These results corroborate the positive correlation between Fe3+ concentration and spin transition pressure in δ-(Al, Fe)OOH at low Fe3+ but imply that there may be a critical Fe3+ concentration at which this effect becomes negligible. The (Al, Fe)-phase H composition studied here contains 7 wt. % Fe3+, which is within the range of iron concentrations in δ-(Al, Fe)OOH studied in Ohira et al. (2019). We would therefore expect the spin transition to occur at a similar pressure (∼35 GPa) if the substitution of Mg and Si did not affect the spin transition pressure. However, the spin crossover inferred from our (Al, Fe)-phase H equation of state occurs at a significantly higher pressure (48–63 GPa) than that in δ-(Al, Fe)OOH and is more similar to that constrained for ε-FeOOH (43–47 GPa; Thompson et al., 2020, 46–54 GPa; Gleason et al., 2013) albeit with a larger width. It is therefore apparent that the dissolution of Mg and Si into the crystal structure of δ-(Al, Fe)OOH has the same effect as increasing the Fe concentration: stabilization of high-spin Fe3+ to higher pressures. The reasons for the persistence of high-spin Fe3+ to higher pressures in (Al, Fe)-phase H relative to δ-(Al, Fe)OOH could be related to differences in ionic radii, to how Mg and Si cations affect the hydrogen bonds in the crystal lattice, and to how strain is accommodated at high pressure.

4.2. Inferring Multiple Transitions in the δ-AlOOH-MgSiO3(OH)2-ε-FeOOH System

The inversion of axial compressibility inferred to be a signature of a hydrogen bond-order disorder transition observed in δ-(Al, Fe)OOH at 10 GPa (Figure 3) is not observed in (Al, Fe)-phase H because hydrogen bonds are disordered in (Al, Fe)-phase H at ambient conditions. Since hydrogen bonds in (Al, Fe)-phase H lie in the a-b plane, strengthening of these bonds is likely to produce noticeable changes in relative compressibilities along the crystallographic axes. In particular, the compressibility along the crystallographic a and b axes is expected to decrease while compressibility along the c-axis remains largely unaffected by changes in hydrogen bonding. At pressures greater than approximately ∼30 GPa, the b-axis becomes significantly less compressible than either the a or c-axis in (Al, Fe)-phase H (Alδ−Fe3+0.07Mg0.02Si1.06OOH) (Figure 3). A decrease in compressibility along the b-axis associated with hydrogen bond order-disorder or symmetrization has also been observed in ε-FeOOH (18 GPa; Thompson et al., 2020, 43 GPa; Gleason et al., 2013), MgSiO3(OH)2 (30 GPa; Nishi et al., 2018), and δ-AlOOH (∼10 GPa; Sano-Furukawa et al., 2018, 2009; 8.2 GPa; Kuribayashi et al., 2014).

The compressional behavior observed here for (Al, Fe)-phase H is similar to that of Fe-Al bearing phase D (MgFe3+0.13Al0.37Si1.4H2Oδ; Chang et al., 2013), although the two compositions are not isostructural (Fe-Al bearing phase D crystallizes in a trigonal structure with space group P31m). The spin transition region inferred from our equation of state is similar to that observed for octahedrally coordinated Fe3+ in Fe-Al bearing phase D (40–65 GPa; Chang et al., 2013). Additionally, the pressure at which the c/a ratio becomes constant in Fe-Al bearing phase D is ∼40 GPa, seemingly unrelated to the Fe3+ spin transition (Chang et al., 2013) and comparable to the ∼35 GPa observed in this study. A relatively constant ratio of a/c reflects similar compressibility along the a and c axes and has been interpreted to be the result of hydrogen bond symmetrization (Chang et al., 2013; Hushur et al., 2011; K. D. Litavsky et al., 2007; Shinmei et al., 2008), although this interpretation was not confirmed by infrared spectroscopy measurements, as discussed in Thompson et al. (2020).

The decrease in compressibility of the b-axis relative to the a and c axes in (Al, Fe)-phase H may instead reflect a change in the how strain is accommodated within the crystal structure. Single crystal X-ray diffraction measurements revealed a change in the mechanism by which strain is accommodated in trigonal α-FeOOH at low (P < 16 GPa) and high (P > 16 GPa) pressure (Xu et al., 2013). That is, at pressures below 16 GPa, strain is accommodated along the channels containing the hydrogen bonds which are parallel to the b-axis and more compressible relative to the Fe3+ octahedra. At pressures greater than 16 GPa, compression of Fe3+ octahedra accommodates a larger proportion of the strain, a change not associated with hydrogen bond symmetrization which occurs at higher pressures. Therefore, the decrease in compressibility of the b-axis in (Al, Fe)-phase H and constant a/c ratio observed in this study at 30–35 GPa may indicate a symmetrization of hydrogen bonds. Alternatively, it may represent a change in the dominant mechanism of strain accommodation within the crystal structure without hydrogen bonds becoming fully symmetric at the same pressure.
The best-fitting model to SMS spectra collected in 24-bunch mode at pressures greater than 35 GPa requires the introduction of a second Mössbauer site for ferric iron (Figure 7). Data collected with access to longer delay times (hybrid mode) require a second Mössbauer site at lower pressures in both compositions (Table 3 and Table S2 and Figure S3 in Supporting Information S1). The significant difference in hyperfine parameters between Mössbauer sites in δ-Fe13 at ∼37 GPa implies a distinct change in the coordination environment and/or the electronic structure of ferric iron. In (Al, Fe)-phase H, the second site at 1.5 GPa could be a result of hydrogen bond disorder. Komatsu et al. (2011) demonstrated that incorporation of Mg and Si into the structure of δ-AlOOH results in disordering of hydrogen bonds and hypothesized that the positions of hydrogen atoms may be affected by the local arrangement of cations. In this context, two Fe$^{3+}$ Mössbauer sites may manifest as a result of two different local arrangements of cations, which may also be important in determining the strength and degree of disordering of hydrogen bonds. This effect may only be observable at low pressures with the longer timing window and more precise measurements conducted in hybrid mode.

The measurements reported here confirm the steep increase in quadrupole splitting of both Fe$^{3+}$ sites in δ-(Al, Fe)-phase H and δ-(Al, Fe)OOH determined from the respective equation of state models. Low-spin fraction of δ-Fe5 and δ-Fe12 is determined by refitting the P-V data reported in Ohira et al. (2019) using the same equation of state parameters (within uncertainty). (b) Normalized stress (P) as a function of normalized strain (f) of (Al, Fe)-phase H and δ-(Al, Fe)OOH.

Figure 8. (a) Fraction of Fe$^{3+}$ atoms in the low-spin state in (Al, Fe)-phase H and δ-(Al, Fe)OOH determined from the respective equation of state models. Low-spin fraction of δ-Fe5 and δ-Fe12 is determined by refitting the P-V data reported in Ohira et al. (2019) using the same equation of state parameters (within uncertainty). (b) Normalized stress (P) as a function of normalized strain (f) of (Al, Fe)-phase H and δ-(Al, Fe)OOH.
the spin transition occurring at similar pressures, as noted in Ohira et al. (2019). The appearance of a second Fe$^{3+}$ Mössbauer site in (Al, Fe)-phase H at the boundary between regions (a) and (b) prior to the spin crossover leads to the conclusion that the second Mössbauer site is unrelated to the spin crossover, at least for (Al, Fe)-phase H. However, a combination of single crystal X-ray diffraction data and infrared spectroscopy measurements at these pressures would better constrain the relationship between hydrogen bond symmetrization and the Fe$^{3+}$ spin crossover in both (Al, Fe)-phase H and δ-(Al, Fe)OOH.

5. Implications

The data presented here reveal that the incorporation of Mg and Si into Fe-bearing compositions in the (δ-AIOOH)-(MgSiO$_3$(OH)$_2$)-(ε-FeOOH) solid solution decreases their compressibility (Figure 9b). Increasing Fe concentration tends to increase the spin transition pressure, at least for low Fe concentrations (<30 wt. %) as does increasing concentration of Mg and Si. In the context of the solid solution, the spin transition pressure shifts to higher pressure with a decreasing proportion of δ-AIOOH. Therefore, we predict that the “Al-rich phase H” samples (Al$_{0.8}$Fe$_{0.2}$Mg$_{0.01}$Si$_{0.02}$)-δ-AlOOH synthesized by X. Liu et al. (2019) would be less compressible and undergo a spin crossover at higher pressures compared to the samples studied here (Al$_{0.8}$Fe$_{0.2}$Mg$_{0.01}$Si$_{0.02}$)-δ-AlOOH. Additional measurements of compressibility and sound velocities on non-end-member compositions within this solid solution are needed to provide quantitative constraints on this prediction and its effects on elastic properties. In particular, if (Al, Fe)-phase H forms due to dehydration processes at the base of the lower mantle (Ohtani, 2020), the cation concentration (and consequently, the sound velocities) may be significantly different from those measured on samples synthesized at pressures and temperatures of the mantle transition zone. Modeling of mid-ocean ridge basalt (MORB) hydration by formation of phases in the (δ-AIOOH)-(MgSiO$_3$(OH)$_2$)-(ε-FeOOH) solid solution may result in increased seismic velocities of hydrous MORB relative to pyrolytic mantle just below the mantle transition zone (~680–900 km; Satta et al., 2021). However, the $\nu_p$ and $\nu_s$ values constrained for δ-(Al$_{0.8}$Fe$_{0.2}$)-δ-AlOOH and used in the modeling for seismic velocities of this solid solution are significantly less than those constrained for compositions with greater concentrations of Fe: (δ-(Al$_{0.8}$Fe$_{0.2}$))-δ-AlOOH; Ohira et al. (2021); (Al$_{0.96}$Fe$_{0.04}$)-δ-AlOOH; Su et al., 2021a; Su et al., 2021b). Comparison of sound velocities predicted by these studies reveal a decrease in both $\nu_p$ and $\nu_s$ with increasing Fe concentration, complicating the modeled seismic signature of MORB hydration and highlighting the need for additional measurements of sound velocities of compositions in the (δ-AIOOH)-(MgSiO$_3$(OH)$_2$)-(ε-FeOOH) solid solution.

Seismological studies have observed the presence of small-scale seismic scatterers in the mid-lower mantle (1,100–1,800 km; 43–78 GPa) and attributed the observed scattering to the presence of basaltic material transported into the lower mantle by a subducting slab (Kaneshima, 2016). For example, Bentham and Rost (2014) observed small-scale scatterers associated with the Mariana slab in the western Pacific to depths of 1,480 km (~65 GPa), as well as at other subduction zones in this region. Similarly, scatterers associated with high-velocity anomalies interpreted to be fossil slabs in the mid-lower mantle (~700–1,600 km) were observed by Rochira et al. (2022) and Saki et al. (2022). Chang et al. (2013) discussed the possibility that seismic scatterers in this...
depth range could be explained by the spin transition of Fe$^{3+}$ in Fe-Al bearing phase D. The spin crossover of (Al, Fe)-phase H (42–60 GPa) spans a similar pressure range as that of Fe-Al bearing phase D (40–65 GPa; Chang et al., 2013), and gives rise to a large decrease in bulk sound velocity over approximately the same depth range (~1,100–1,550 km). However, the synthesis experiments of X. Liu et al. (2019) demonstrated that Fe-Al bearing phase D transforms to Fe-Al bearing phase H above 25 GPa and 1000°C, possibly by the reaction: Fe-Al bearing phase D + garnet = Fe-Al bearing phase H + bridgmanite + davemaite (Tschauner et al., 2021). At pressures of the spin crossover of Fe$^{3+}$, (Al, Fe)-phase H is therefore more likely to form as the stable hydrous phase in Earth’s mantle. While this study constrains the pressures of the spin transition at ambient temperature, first-principles calculations of the temperature dependence of the spin transition of Fe$^{3+}$ in the NAL phase suggests that the spin crossover region may broaden with increasing temperature, but not change pressure appreciably (Hsu, 2017).

Modeling of seismic velocities of the major constituents of metabasalt, formed from recycled mid-ocean ridge basalt suggests that a thin layer (<10 km) of a metabasaltic aggregate within a subducting slab could scatter seismic waves on the observation that S wave velocity ($v_S$) in metabasalt could be ~2–4% lower than $v_S$ in pyrolite at the top of the lower mantle (Tsuchiya, 2011), resulting in a significant change in $v_S$ over a relatively short length scale (<10 km). In (Al, Fe)-phase H, $v_S$ may be invariant to pressure across the spin transition and lower than that of ambient mantle at these pressures whereas the P wave velocity ($v_P$) is expected to decrease, by analogy to sound velocities reported for $\delta$-(Al, Fe)OOH (Ohira et al., 2021). The concentration of (Al, Fe)-bearing phase H in subducted oceanic crust between 1,100 and 1,550 km could enhance scattering of seismic waves in this region via significant reduction of $v_S$ in metabasaltic rocks which are otherwise indistinguishable from pyrolitic mantle by $v_S$ in this depth range (Tsuchiya, 2011). However, measurements of the S wave speed in (Al, Fe) phase H are needed, as well as more precise constraints on the shape and elastic parameters are necessary to better understand scatterers in the lower mantle (Kaneshima, 2016) and formulate a quantitative interpretation of their origin.

Large, low seismic velocity provinces (LLSVPs) are basal mantle structures which may be thermochemical in nature and are defined by negative shear-wave velocity anomalies that are anti-correlated with positive bulk sound velocity anomalies (Garnnero et al., 2016; McNamara, 2019). One possible source of chemical heterogeneity is the transport of subducted material carried into the lowermost mantle by slabs (Garnnero et al., 2016; Jones et al., 2020; McNamara, 2019; Ohtani, 2020). $\delta$-(Al, Fe)OOH, MgSiO$_3$(OH)$_2$, and (Al, Fe)-phase H each represent positive perturbations in bulk sound velocity ($v_P$) relative to PREM (Figure 9c). Assuming the same thermal parameters as determined for $\delta$-AlOOH, a smaller proportion of (Al, Fe)-phase H (1–4 wt.%) than $\delta$-(Al, Fe)OOH (6–8 wt.%) (Ohira et al., 2019) is necessary to produce the $v_P$ anomalies observed at the edges of LLSVPs. This small concentration of (Al, Fe)-phase H is 10%–14% less than the proportion of (Al, Fe)-phase H in the ($\delta$-AlOOH)-(MgSiO$_3$(OH)$_2$)-(Fe-OOH) system produced by synthesis experiments on hydrous oceanic basalts at pressures of 25–27 GPa and temperatures between 1273 and 1473 K (X. Liu et al., 2019). If an anti-correlation of $v_P$ and $v_S$ is observed in (Al, Fe)-phase H, as in $\delta$-(Al, Fe)OOH, accumulation of this phase as part of subducted basaltic material may contribute to the positive bulk sound velocity and negative shear wave velocity anomalies observed near the edges of LLSVPs.

Data Availability Statement
Data used to support the findings of this work can be accessed through the California Institute of Technology Research Data Repository. The data set (Strozewski et al., 2022) is accessible at https://doi.org/10.22002/6mcgx-p9474.

References