# Quenchable water-rich aluminous post-stishovite: implications for water and seismic scatterers in the lower mantle

R. Myhill, D. J. Frost, T. Boffa-Ballaran, H. Bureau, C. Raepsaet

*Bayerisches Geoinstitut, Universität Bayreuth, Universitätsstrasse 30, 95447 Bayreuth, Germany*

**Abstract**

Seismic scatterers

ULVZs by seifertite formation?

Geochemistry

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## 1. Introduction

The stishovite structure (tetragonal, P$4_2$/mnm, no. 136) undergoes a weak first-order transition (Andrault et al., 1998; Hemley et al., 2000) with second-order characteristics of Landau/ferroelastic type (Tsuchida and Yagi, 1989; Carpenter et al., 2000) to the $CaCl_2$-type structure (orthorhombic, Pnnm, no. 58). This transition occurs at pressures of ∼50 GPa at room temperature (Kingma et al., 1995; Andrault et al., 1998), increasing with temperature to ∼70 GPa at 2200 K (Hirose et al., 2005; Nomura et al., 2010). A somewhat higher dT/dP was observed by Ono et al. (2002). The nature of this transition means that the shear modulus $C_{11}$ - $C_{12}$ decreases with increasing pressure and vanishes at the transition pressure, as observed in spectroscopic and high pressure diffraction studies (Kingma et al., 1995; Shieh et al., 2002). The stishovite-post-stishovite

*Corresponding author: R. Myhill
*Email address:* myhill.bob@gmail.com (R. Myhill, D. J. Frost, T. Boffa-Ballaran, H. Bureau, C. Raepsaet)

transition is therefore of interest to seismologists, as it should produce zones of low shear wave velocity which act as scatterers in the deep mantle.

Deviatoric stresses in the diamond anvil cell can cause large variations in the pressure of the stishovite to post-stishovite transition. Nonhydrostaticity greatly decreases the transition pressure from 60 GPa (Andrault et al., 2003; Hemley et al., 2000) to 40 GPa (Kingma et al., 1996; Singh et al., 2012). Molecular and lattice dynamic studies suggest that only 1.5–2.5 GPa differential stress is required to cause this decrease in pressure (Dubrovinsky and Belonoshko, 1996).

Aluminium has a profound effect on the stability of the post-stishovite phase. $Al_2O_3$ can be incorporated into stishovite by the substitution of Si by Al with the formation of oxygen vacancies (Smyth et al., 1995; Hirose et al., 2005; Bromiley et al., 2006; Lakshtanov et al., 2007a):

$$2Si_{Si}^{x} + O_{O}^{x} + Al_2O_3 \rightarrow 2Al_{Si}^{/} + V_{\ddot{O}} + 2SiO_2 \tag{1}$$

An alternative mechanism, where charge balance is accomplished by Al occupying the large interstitial sites is probably minor Smyth et al. (1995):

$$3Si_{Si}^{x} + 2Al_2O_3 \rightarrow 3Al_{Si}^{/} + Al_{i}^{\cdots} + 3SiO_2 \tag{2}$$

It has been argued that the addition of 4 wt% $Al_2O_3$ in the absence of any other components causes the transition to shift from 50 to 23 GPa at room temperature by inducing a 'chemical pressure' (Bolfan-Casanova et al., 2009). In stishovite, there is one octahedral cation position (Wyckoff notation 2a) located at the origin and the body center of the tetragonal cell. One oxygen at position 4f creates a moderately distorted octahedron with point symmetry mmm. The addition of Al *decreases* distortion of this octahedron (Smyth et al., 1995). The addition of Al should therefore have little effect on the stishovite-post-stishovite transition (Panero, 2006). The results of Bolfan-Casanova et al. (2009) are therefore unexpected; it seems possible that another component (such as $H_2O$) or deviatoric stress acted to stabilise the $CaCl_2$ structure.

It has also been suggested that the coupled substitution of Al and H may have a significant effect on the transition pressure. Lakshtanov et al. (2007b) have shown that the addition of 6 wt% $Al_2O_3$ and 0.24 wt% $H_2O$ reduces the transition pressure to 24 GPa at room temperature. The substitution mechanism in this case is probably

$$2Si_{Si}^{x} + Al_2O_3 + H_2O \rightarrow 2Al_{Si}^{/} + 2H_i^{\cdot} + 2SiO_2 \qquad (3)$$

Given that high pressure $\delta$-AlOOH is isostructural with the post-stishovite phase above ca. 19 GPa (Sano-Furukawa et al., 2008; Kuribayashi et al., 2014), after transforming from the $P2_1nm$ structure (no. 31) (Suzuki et al., 2000; Komatsu et al., 2006; Vanpeteghem et al., 2007), it seems sensible to suggest that addition of an AlOOH component lowers the transition pressure. Ab initio calculations support this suggestion (Umemoto et al., 2015). The equilibrium transition for 6.25 mol% AlOOH is at ca. 15 GPa at room temperature, implying an even more marked reduction than observed in the experimental data (Lakshtanov et al., 2007b). This could be due to inaccuracies in the ab-initio data, or metastable preservation of the tetragonal phase in the experiments. Umemoto et al. (2015) also suggest that the larger number of hydrogen sites stabilises the tetragonal structure at high temperatures, changing the slope of the transition. The tetragonal → orthorhombic transition in their simulations is associated with splitting of the hydrogen sites on the equatorial oxygens into two groups, one occupied and the other unoccupied. Additionally, the redistribution of hydrogens among equatorial oxygens in the tetragonal → orthorhombic transition implies that it is now first order and no longer ferroelastic. Anelasticity by hydrogen hopping seems a plausible alternative to reduce seismic body wave speeds.

Despite this, $H_2O$ contents in tetragonal stishovite measured using the FTIR calibration of Pawley et al. (1993) are less than 20% of that expected from an AlOOH component (Panero et al., 2003; Bromiley et al., 2006; Litasov et al., 2007) and in MORB compositions (Chung and Kagi, 2002).

This study was designed to investigate water solubility in Al-rich stishovite by synthesising crystals at relatively high temperature (Ono, 1999). In doing so, we created and quenched an Al-H rich post-stishovite phase.

### *1.1. Hysteresis vs. stabilisation*

(Umemoto et al., 2015)

### *1.2. Mechanism of shear wave velocity reduction*

Ferroelasticity (Carpenter et al., 2000) Snoek relaxation (anelasticity via H mobility) (Snoek, 1941; Nowick and Berry, 1972; McKnight et al., 2007).

### *1.3. Mechanisms of Al-, H incorporation*

We found that hydrogen was most stable when bonded to the apical oxygen of the Al-octahedron, with the hydroxyl bond along $\langle 110 \rangle$ and co-planar with Al (Panero and Stixrude, 2004).

The relatively short O-O distance and correspondingly long O-H distance in the stishovite-AlOOH solid solution would lead one to expect a low OH stretching frequency compared to other nominally anhydrous minerals, consistent with the value of 3111 $cm^{-1}$ observed by Pawley et al. (1993).

Symmetric bonding (Panero and Stixrude, 2004)

### *1.4. Water concentrations in stishovite*

Pawley et al. (1993) calibration Panero et al. (2003) Bromiley et al. (2006), Litasov et al. (2007), MORB Chung and Kagi (2002),

### *1.5. Elastic properties*

Andrault et al. (2003) Lakshtanov et al. (2005) Ono et al. (2002) Sano-Furukawa et al. (2009)

### *1.6. Phase relations in the lower mantle*

Irifune and Ringwood (1993) Wood (2000) Hirose (2002) Walter et al. (2015) Litasov and Ohtani (2005)

### 1.7. Datasets and modelling

Holland and Powell (2011) Stixrude and Lithgow-Bertelloni (2011) Cottaar et al. (2014)

#### 1.7.1. Elastic properties AlOOH

Suzuki (2009) (Sano-Furukawa et al., 2008) Vanpeteghem et al. (2002) Tsuchiya and Tsuchiya (2009) Li et al. (2006)

## 2. The solid solution (MgSi, $Fe^{2+}$Si, $Fe_2^{3+}$, $Al_2$)$O_4H_2$

### 2.1. Endmembers

#### 2.1.1. $SiO_2$

#### 2.1.2. δ-AlOOH

#### 2.1.3. δ-FeOOH

Pnma (no.62 $\alpha$) to $P2_1nm$ (no. 31, $\varepsilon$) (Gleason et al., 2008) to Pnnm (no. 58, high spin) to Pnnm (no. 58, low spin) (Gleason et al., 2013)

#### 2.1.4. "Phase H"

The addition of an $MgSiO_4H_2$ component also stabilises the Pnnm structure in stishovite (Komatsu et al., 2011). A previous candidate space group (Pnn2; no. 34 Kudoh et al., 2004) is now thought to be unlikely.

Stability (Ohtani et al., 2014) Ab initio P2/m (no. 10) (Tsuchiya, 2013) Pnnm (no. 58) (Bindi et al., 2014) $P2_1nm$ (no. 31) (Nishi et al., 2014)

Kudoh et al. (2004) suggested a hypothetical high pressure form of $Mg(OH)_2$ also in the space group Pnnm from Mg incorporation. Importance of the AlOOH - phase H solid solution Ohira et al. (2014)

## 3. Other phases

Ohtani (2015)

### 3.1. *Water in seifertite*

Post-stishovite undergoes a phase transition to the mineral seifertite with the scrutinyite ($\alpha$-$PbO_2$) structure (orthorhombic, Pbcn, no. 60 or Pb2n) at about 120-140 GPa and 2000-2500 K (Murakami et al., 2003; Grocholski et al., 2013). The addition of aluminium under dry conditions may stabilise seifertite to 110 GPa at 2000 K (Hirose et al., 2005), although this remains controversial (Grocholski et al., 2013). The effect of hydrogen on the structure is currently unknown. As there are no hydrous phases known with the seifertite structure, the addition of water probably destabilises seifertite relative to post-stishovite. This supposition is supported by the lack of water in the isostructural $TiO_2$ (II) phase, which contains negligible water (Bromiley et al., 2004).

$\delta$-AlOOH remains stable throughout the lower mantle, and probably transforms to a cubic structure ($Pa\bar{3}$) at core pressures (Tsuchiya and Tsuchiya, 2011).

### 3.2. *$\delta$-$Al(OH)_3$*

$P2_12_12_1$ (no. 19) to Pnma (no. 62) at $\sim$67 GPa Matsui et al. (2011). Xue and Kanzaki (2007)

### 3.3. *Ca-perovskite*

Tetragonal (probably P4/mmm, no. 123) (Shim et al., 2002) $\rightarrow$ Cubic (Pm3m) for low Al contents. For pure $CaSiO_3$, transition occurs at ca. 580 K at 50 GPa (Kurashina et al., 2004; Komabayashi et al., 2007)

Orthorhombic (Pbnm) $\rightarrow$ Cubic (Pm3m) for Al-rich $CaSiO_3$ (Kurashina et al., 2004). At 5.9 wt%, transition occurs at ca. 1840 K at 50 GPa (Kurashina et al., 2004).

In a pyrolitic mantle composition, the $CaSiO_3$ perovskite contains 1.0–2.3 wt.% $Al_2O_3$ at upper mantle pressures and somewhat less (0.7–1.6 wt.%) at lower mantle pressures (Kesson et al., 1998; Wood, 2000; Hirose, 2002)

In a MORB composition, 2.0–4.8 wt.% and 1.2–4.5 wt.% $Al_2O_3$ are included in $CaSiO_3$-rich perovskite in garnetite and perovskitite lithologies, respectively (Kesson et al., 1994; Irifune and Ringwood, 1993; Hirose and Fei, 2002).

### *3.4. Reaction with metal*

(Terasaki et al., 2012)

## 4. Lower mantle scatterers

Deuss et al. (2013) Kaneshima and Helffrich (1998, 2003) Niu et al. (2003) Krüger et al. (2001) Kaneshima (2009) Bina et al. (2010) Kaneshima et al. (2010) Bentham and Rost (2014) Asahara et al. (2013) Mookherjee (2011)

## 5. Experimental and analytical techniques

## 6. Chemical composition

Figure 1: Single crystal XRD spectra of post-stishovite

## 7. Conclusions

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