Thermoelasticity of phase D and implications for low-velocity anomalies and local discontinuities at the uppermost lower mantle

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Abstract

Phase D is a potential water carrier in the slab subducted to the uppermost lower mantle (ULM) and its velocity and density characteristics are important for seismological detection of water cycle in the deep Earth. Here we obtained the density and velocities of phase D under the conditions of the ULM using first-principles calculations based on the density functional theory. In contrast to previous results, both hydrogen bond symmetrization and the corresponding abrupt increase in bulk modulus are absent in the optimized structure up to 80 GPa. The velocities of phase D are higher than those of periclase and only slightly lower than those of bridgmanite by 0.5%–3.5% for VP and by 0%–2.0% for VS in the ULM (660–1000 km), thus the accumulation of phase D can hardly produce obvious low-velocity anomaly in the ULM observed by seismological studies, but it may contribute significantly to the seismic anisotropy because of its strong elastic anisotropy.

Phase D will dehydrate into bridgmanite and stishovite at the depth of ~700–1200 km. The velocity jumps are 6.6% for VP and 5.1% for VS at the depth of 660 km but reduce to 2.3% and 0.3% at the depth of 1000 km, respectively. However, phase D is ~15% less dense than bridgmanite, so the dehydration of phase D could still produce large impedance jumps in the ULM, which may account for some discontinuities observed at the depth of ~1000–1200 km in subduction zones.
This study

Frost99
Shinmei08
Wu16

Yang97 Ohtani97 Frost99 Shinmei08 Hushur11 Rosa12 Rosa13a Rosa13b Wu16 Xu20+Al Xu21

(a) Unit-cell Volume (Å³)

(b) Length and Volume Changes

Pressure (GPa)

Static

300 K 700 K 1100 K 1500 K 2000 K

This study

Frost99 Shinmei08 Rosa13a Wu16

a/a₀  c/c₀  v/v₀
Hosted file

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Key Points:

• Elasticity and density of phase D under the lower-mantle conditions are obtained using first-principles calculations
• Accumulation of phase D may account for seismic anisotropy rather than low-velocity anomalies in the uppermost lower mantle (ULM)
• Decomposition of phase D in the ULM causes a density jump, possibly explaining some discontinuities in subduction zones

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Abstract

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Phase D will dehydrate into bridgmanite and stishovite at the depth of $\sim 700–1200$ km. The velocity jumps are 6.6% for $V_P$ and 5.1% for $V_S$ at the depth of 660 km but reduce to 2.3% and 0.3% at the depth of 1000 km, respectively. However, phase D is $\sim 15\%$ less dense than bridgmanite, so the dehydration of phase D could still produce large impedance jumps in the ULM, which may account for some discontinuities observed at the depth of $\sim 1000–1200$ km in subduction zones.

Plain Language Summary

Water can be transported into the deep mantle through dense hydrous minerals by subduction slabs, some of which could be detected through geophysical observations because of their distinct physical properties, such as low seismic velocity and high electrical conductivity. Phase D is one of the important hydrous minerals in the uppermost lower mantle (ULM), but its elastic properties at the lower mantle conditions remain unclear. In this study, we obtain the elasticity and density of phase D under the conditions of the ULM. The velocities of phase D are comparable to those of major minerals in the ULM, so the enrichment of phase D is not likely to generate seismically detectable low-velocity anomaly, but the strong elastic anisotropy of phase D may explain some seismic anisotropy observations. Our results also show that the dehydration of phase D into bridgmanite and stishovite in the ULM produces negligible velocity contrasts but a prominent density increase, which could account for some seismic discontinuities with large density contrasts in the ULM.

1 Introduction

Water in the Earth’s interior exerts significant influences on the geochemical evolution and mantle dynamics because a small amount of water can significantly change the rheological properties, melting temperature, and diffusion rate of materials (Hirschmann, 2006; S.-i. Karato & Jung, 2003; Mei & Kohlstedt, 2000). There is significant amounts of evidence for the occurrence of water in the deep mantle. It has been shown that wadsleyite and ringwoodite, candidate nominally anhydrous minerals in the mantle transition zone (MTZ), could incorporate several weight percent of H$_2$O (Bell & Rossman, 1992; Inoue et al., 1995, 2010; Jacobsen et al., 2005; Smyth, 1987), whilst the hydrous ringwoodite and ice-VII discovered in superdeep diamonds (Pearson et al., 2014; Tschauner et al., 2018) provide direct evidence for the existence of the non-negligible amount of H$_2$O in the deep mantle. Water can be likely transported into the MTZ and the lower mantle via subducting slabs through the formation and dehydration of dense hydrous magnesium silicates (DHMSs) (Angel et al., 2001). Some geophysical anomalies, such as high $V_P/V_S$, high electrical conductivity, and low-velocity anomalies, were interpreted as locally high water content released by the dehydration of DHMSs (S.-i. Karato, 2011; J. Li et al., 2013; Savage, 2012) or merely their existence owing to their low-velocity characteristics (Z. Liu et al., 2016; Schmandt et al., 2014; D. Yang et al., 2017). Meanwhile, the generation/breakdown of DHMSs could cause considerable impedance contrasts, giving rise to seismic discontinuities. For example, the
decomposition of a small amount of superhydrous phase B could explain the 800-km discontinuity in western Pacific subduction zones (D. Yang et al., 2017), and the dehydration of phase H could produce significant seismic impedance increase in the mid-mantle (Song et al., 2022). Combining these seismological observations with the velocity and density characteristics, phase transitions, and corresponding impedance contrasts of DHMSs could help constrain the water content in the deep interior and provide insights into the circulation of water in the whole Earth.

Phase D is considered as a significant carrier of water in slabs subducted to the uppermost lower mantle (ULM). The ideal chemical formula of phase D is MgSi$_2$H$_2$O$_6$ containing 10 wt.% water, whereas the synthesized phase D shows a wide variation in Mg/Si from 0.53 to 0.71 and the water content varies from 10 wt.% to 18 wt.% (Chang et al., 2013; D. Frost & Fei, 1999; Hushur et al., 2011; Litasov et al., 2007; Rosa et al., 2012; Rosa, Mezouar, et al., 2013; Shinmei et al., 2008; X. Wu et al., 2016; Xu et al., 2020; Xu, Li, et al., 2021; H. Yang et al., 1997). Many hydrous phases exhibit low velocities (X. Li et al., 2016; Mao et al., 2012; Rosa et al., 2012, 2015; D. Yang et al., 2017) and could be identified by seismic observations. The weight fraction of phase D can be as high as 57% in hydrous peridotite (Ohtani et al., 2004), which is also possible to generate seismic velocity anomalies in the MTZ and the ULM. On the other hand, phase D will dehydrate into bridgmanite and stishovite at the temperature of around 1500 K and a wide depth range of ∼700–1200 km (Nishi et al., 2014). Correspondingly, many seismic studies have detected discontinuities exhibiting large impedance contrasts at the depth of ∼800–1200 km in subduction zones (Courtier & Revenaugh, 2008; Schumacher & Thomas, 2016; Waszek et al., 2018). There may exist a connection between these discontinuities and the dehydration of phase D, and the velocities and density of phase D under the lower mantle conditions are crucial for deciphering its role in such seismic observations.

The crystal structure and equation of state of phase D have been widely studied (D. J. Frost & Fei, 1998; D. Frost & Fei, 1999; Hushur et al., 2011; Kudoh et al., 1997; Litasov et al., 2007; L.-g. Liu, 1993; L.-G. Liu et al., 1998; Rosa et al., 2012; Rosa, Mezouar, et al., 2013; Shieh et al., 2009; Shinmei et al., 2008; X. Wu et al., 2016; Xue et al., 2008; H. Yang et al., 1997) and the elastic properties of Mg-endmember have also been investigated by first-principles calculations at static conditions (Mainprice et al., 2007; Tsuchiya & Tsuchiya, 2008) and Brillouin scattering and ultrasonic measurements at ambient conditions (L.-g. Liu et al., 2004; Rosa et al., 2012; Xu, Li, et al., 2021). The sound velocities of Al-bearing phase D up to 22 GPa and 1300 K were also determined by ultrasonic measurements (Xu et al., 2020). However, there are no elasticity data of Mg-phase D under both high-temperature and high-pressure conditions. In this contribution, we obtained the elastic properties of Mg-endmember phase D (MgSi$_2$H$_2$O$_6$) and its velocity and density characteristics under the lower mantle conditions using first-principles calculations within the generalized gradient approximation. Combining our results with available data of other minerals, we calculated the velocity and impedance contrasts caused by its dehydration and discussed its close relationship to seismic observations in the ULM.

2 Computational Detail

The ideal structure of phase D (MgSi$_2$H$_2$O$_6$) is trigonal with MgO$_6$ and SiO$_6$ octahedra in two separate layers stacked along the c-axis. The OH bonds of phase D are located between adjacent octahedra in the MgO$_6$ layer and the hydrogens are only 33% occupied (Xue et al., 2008; H. Yang et al., 1997). To maintain the symmetries of phase D, we constructed the same supercell as adopted in Mainprice et al. (2007) with edges a-b, a+2b, and c to perform first-principles calculations and the space group is $P\overline{3}m1$.

All calculations in this study were performed based on the density functional theory (DFT) using the open-source quantum espresso package (Giannozzi et al., 2009) with the Generalized Gradient Approximation (GGA) (Hamann, 1997; Perdew et al., 1996). The
energy cutoff for the plane wave was set to 70 Ry. Structural optimizations were performed using the variable cell-shape damped molecular dynamics method (Wentzcovitch et al., 1993) at certain pressures with a k-point mesh of 6×6×6, and the density functional perturbation theory (Baroni et al., 2001) was used to calculate the dynamical matrices with a 4×4×4 q-point mesh. The thermal elasticity of phase D was calculated using a semianalytical method developed by Z. Wu and Wentzcovitch (2011), similar to previous studies (Hao et al., 2019; Qian et al., 2018; Wang et al., 2019, 2021; Z. Wu & Wang, 2016; D. Yang et al., 2017; Yao et al., 2018; Zou et al., 2018).

3 Results

3.1 Thermodynamic Properties

The calculated equations of state of phase D are shown together with the experimental measurements in Figure 1a. The differences among experiments primarily result from the wide variations in Mg/Si ratio, aluminum content, and water content in the synthesized phase D. Except the Al-bearing phase D (Xu et al., 2020), most measured volumes (D. Frost & Fei, 1999; Hushur et al., 2011; Ohtani et al., 2004; Rosa et al., 2012; Rosa, Mezouar, et al., 2013; Rosa, Sanchez-Valle, et al., 2013; Shinmei et al., 2008; X. Wu et al., 2016; Xu, Li, et al., 2021; H. Yang et al., 1997) are slightly smaller than our calculated results due to the overestimation of GGA calculation, but there is much better consistency in the relative change of volume (V/V0) with pressure (Figure 1b). Our calculated results lie between the experimental data of Shinmei et al. (2008) and X. Wu et al. (2016) within a broad pressure range (Figure 1b) and agree with those of Rosa, Mezouar, et al. (2013) at all pressures (Figure 1b). Furthermore, the calculated relative changes in cell parameters are also consistent with the experimental results. In comparison with the absolute values at different pressures, the relative changes in volume (V/V0) and lattice constants (a/a0, c/c0) play a more important role in the determination of the compressional properties.

The calculated thermal expansion (α = 1/V ∂V/∂T) of phase D as well as the experimental data (Shinmei et al., 2008) are shown in Figure 2a. The black dashed line represents the experimental results at 0 GPa (Shinmei et al., 2008), which are larger than our calculated results. The thermal expansion of Shinmei et al. (2008) was calculated using the high-temperature Birch-Murnaghan equation of state (HTBM EOS) based on the P-V-T data of phase D. It should be noted that there are only two room-temperature volume data points at ambient pressure in their study, whereas most of the data were measured at 17–46 GPa. Therefore, their thermal expansion of phase D at high pressures should be more convincing than that at 0 GPa. As shown in Figure 2a, these high-pressure data agree better with our calculated results. The calculated thermal Gruneisen parameter, heat capacity at constant volume (Cv) and constant pressure (Cp) are also shown in Figure 2.

3.2 Thermal Elastic Properties

The elastic tensor of phase D with a trigonal symmetry can be totally determined by six independent elastic constants (C11, C13, C12, C13, C44, and C14). The calculated thermal constants, adiabatic bulk (Ks) and shear (G) moduli, longitudinal (Vp) and shear wave (Vs) velocities, as well as the experimental data (Rosa et al., 2012; Xu et al., 2020; Xu, Li, et al., 2021), are shown in Figure 3. The first and second derivatives of elastic moduli M (M = Cij, Ks, and G) with respect to pressure and temperature are shown in Table S1 and Table S2, respectively. The calculated compressional elastic constants (C11 and C13) and shear elastic constant (C44) are slightly larger than the experimental results (Rosa et al., 2012), whereas the off-diagonal elastic constants (C12, C13, and C14) are a little smaller (Figure 3a and 3b). Since there are no high-pressure experimental data of the elastic constants of phase D, we compared the linear compressibility calculated from our elastic constants with that from the lattice constants of experimental data and they exhibit good consistency (Text S1; Figure S1).
The adiabatic bulk moduli ($K_S$) are in good agreement with the experimental results of Rosa et al. (2012) and slightly larger than that of Xu et al. (2020) and Xu, Li, et al. (2021), but our shear moduli ($G$) are significantly larger than all experiments, especially Xu, Li, et al. (2021) (Figure 3c). The deviations probably result from different Al and H$_2$O contents in phase D. Phase D in this study contains 10 wt.% H$_2$O, whereas the synthesized samples in Rosa et al. (2012) and Xu, Li, et al. (2021) include 12.1 and 16.1 wt.% H$_2$O, respectively, and the sample in Xu et al. (2020) contains both 18.8 wt.% Al$_2$O$_3$ and $\sim$16.0 wt.% H$_2$O. The negative correlation between H$_2$O content and elastic moduli is consistent with many minerals, such as wadsleyite and ringwoodite (Wang et al., 2019, 2021), but the effect of aluminum content on the elastic moduli of phase D requires further investigation. Since the density of phase D in this study is close to these experiments and the compressional and shear wave velocities are expressed by $V_P = \sqrt{(K_S + \frac{4}{3}G)/\rho}$ and $V_S = \sqrt{G/\rho}$, the larger shear moduli in our results further lead to higher velocities (Figure 3d). The $V_P$ and $V_S$ of phase D in this study are 2.9% and 5.7% larger than that in Rosa et al. (2012) at ambient conditions and approximately 4–6% and 8–9% larger than that in Xu, Li, et al. (2021) at pressures of 3–13.6 GPa, respectively, exhibiting the significant effect of various water contents.

Previous theoretical studies (Tsuchiya et al., 2005; Tsuchiya & Tsuchiya, 2008) suggested that the hydrogen bond symmetrization (HBS) (the H atom is located at the middle point of two neighboring O atoms) would occur in phase D at 40 GPa, causing a $\sim$20% increase in the bulk modulus. However, HBS is absent in our optimized structures up to 80 GPa (Figure 4) and such an increase in the bulk modulus is not observed in this study and Mainprice et al. (2007). The discrepancy may be caused by different structure models of phase D. The structure in Tsuchiya et al. (2005) is distorted from trigonal symmetry and has a triclinic unit cell due to the fractional occupancy of hydrogen. To solve this problem, Mainprice et al. (2007) constructed a corresponding supercell with the space group $P\overline{3}m1$ (adopted in this study) instead of $P\overline{3}1m$. Despite this discrepancy, infrared spectroscopic studies on phase D observe neither significant changes in the frequency or intensity of OH stretching vibrations nor the merging of the separate OH peaks with increasing pressure up to 42 GPa (Shieh et al., 2009). Moreover, no direct experimental results hitherto indicate that the bulk modulus of phase D will increase abruptly around 40 GPa. The dramatic increase in bulk modulus observed by Hushur et al. (2011) probably results from the assumption that $K_0^\prime$ (the pressure derivative of the bulk modulus at 0 GPa) is 4, whereas both Rosa et al. (2012) and this study obtain a value close to 5, significantly larger than their estimate and that of major minerals in the MTZ and lower mantle.

### 3.3 Anisotropy

The elastic wave velocities of single crystal usually exhibit variations along different crystallographic orientations and the single-crystal anisotropy can be defined as in Karki et al. (2001):

$$A_P = 2 \times \frac{V_{P,\text{max}} - V_{P,\text{min}}}{V_{P,\text{max}} + V_{P,\text{min}}}$$

$$A_S = 2 \times \frac{V_{S,\text{max}} - V_{S,\text{min}}}{V_{S,\text{max}} + V_{S,\text{min}}}$$

$$A_{Po} = 2 \times \frac{(V_{S1} - V_{S2})_{\text{max}}}{V_{S1} + V_{S2}}$$

where $A_P$, $A_S$ and $A_{Po}$ represent the $V_P$, $V_S$, and $V_S$ polarization anisotropies, respectively. $V_P$, $V_{S1}$, and $V_{S2}$ represent the wave velocities along a given crystallographic orientation, which can be calculated using the Christoffel equation (Musgrave, 1970):
Here $C_{ijkl}$ refers to the fourth-ranked elastic tensor and the unit vector $n = (n_1, n_2, n_3)$ is the propagation direction of the elastic wave. $V$ and $\rho$ represent velocity and density, respectively.

The $V_S$ wave polarization anisotropy of phase D is significantly large (approximately 18%) in the MTZ and the ULM (Figure 5). Rosa, Sanchez-Valle, et al. (2013) indicate that phase D exhibits a relatively low strength under uniaxial compression and tends to develop lattice preferred orientations under plastic flow. They also estimated that 16 vol.% of phase D in hydrous subducted peridotite could explain the shear wave splitting (0.9±0.3%) and the shear wave ray polarization geometry observed in a detached fragment of the Tonga slab below the MTZ (Chen & Brudzinski, 2003). Our calculated anisotropies of phase D are similar to those in Rosa et al. (2012) (Figure 5), further corroborating this interpretation.

4 Discussions

4.1 The Velocities and Density Characteristics of Phase D in the MTZ and ULM

The seismic velocities and density of phase D, ringwoodite, periclase, bridgmanite, and stishovite along a cold geotherm are shown in Figure 6. Similar to other hydrous phases, phase D shows an obvious low-density feature, especially at the ULM, and the density contrast between phase D and bridgmanite is up to 15%, thus its presence could contribute to the stagnation of slabs at the depth of ~600–1000 km (Fukao et al., 2009) to a large extent. The velocity characteristics, however, are quite different. Unlike other hydrous phases, phase D shows relatively high wave velocities in the MTZ, and the velocities of phase D increase much faster with pressure than those of candidate minerals in the MTZ and ULM (Figure 6) due to its large pressure derivatives of $K_S$ and $G$ (Table S1). Its $V_P$ and $V_S$ are 1.5%–3.0% and 6.8%–9.1% higher than those of ringwoodite at depths of ~500–660 km, respectively. Stishovite, one of the dehydration products of phase D (Nishi et al., 2014) and an important component in the oceanic crust, has significantly high velocities in the MTZ. The velocity contrasts between phase D and stishovite are 14.1%–18.6% for $V_P$ and 10.8%–13.5% for $V_S$ in the MTZ. However, due to the softening of the shear modulus of stishovite (Karki et al., 1997; R. Yang & Wu, 2014) and the large pressure dependence of velocities of phase D, the $V_P$ and $V_S$ of stishovite are only 5.6% and 1.6% higher than those of phase D at the depth of 1000 km, respectively, which become even smaller at larger depths. Similarly, although phase D exhibits much lower velocities than bridgmanite at ambient conditions as in Rosa et al. (2012), the velocity contrasts between phase D and bridgmanite are not prominent for both $V_P$ (~0.5%–3.5%) and $V_S$ (~0%-2%) within the depth range of ~660–1000 km (Figure 6). This indicates that the accumulation of phase D can hardly produce an obvious low-velocity anomaly in the ULM observed in seismological studies (Brudzinski & Chen, 2003; Z. Liu et al., 2016), which is inconsistent with the conclusion at ambient conditions (Rosa et al., 2012). However, as mentioned above, the velocities of phase D are negatively correlated with the $H_2O$ content, so a higher $H_2O$ content may increase the possibility of generating low-velocity anomalies, but it still requires more quantitative investigations on the effect. Xu et al. (2020) used the data of Al-bearing phase D, which include 18.8 wt.% $Al_2O_3$ and ~16.0 wt% $H_2O$, to calculate the velocities and density contrasts between the dry and hydrous harzburgite, indicating that the hydrous harzburgite with ~1.2 wt.% $H_2O$ only exhibits slightly lower velocities at the ULM, -0.5% and -1.0% for $V_P$ and $V_S$ respectively, hardly accounting for the -3% velocity anomalies for both $V_P$ and $V_S$ in Tonga slab (Brudzinski & Chen, 2003), although the Al-bearing phase D has lower velocities than ours under such conditions (Figure 3d). This could provide an approximate estimation on the $H_2O$ effect, that is, such a water content is not enough to cause obvious low-velocity anomalies, but the contribution of Al to the velocities remains to be explored.
In contrast, superhydrous phase B, another stable hydrous mineral in cold slabs in the ULM, may account for low-velocity observations. It has much lower velocities than bridgmanite and periclase, and the released water by its dehydration at the depth of ~800 km should migrate upwards, causing the partial melt to reduce the velocity at a shallower depth (D. Yang et al., 2017). However, superhydrous phase B has negligible anisotropy compared with phase D under such conditions, which cannot explain the observed seismic anisotropy in the same region (Chen & Brudzinski, 2003). Therefore, the low-velocity anomaly could be mainly caused by superhydrous phase B, whereas the presence of phase D could primarily account for the seismic anisotropy. In addition, it has been found that phase D and superhydrous phase B are likely to coexist in the ULM (Nishi et al., 2014; Xu, Inoue, et al., 2021), further supporting both observations in the same region.

4.2 The Dehydration of Phase D and Implications on Discontinuities in the ULM

Besides the global 410-km and 660-km discontinuities, seismological studies detected many local discontinuities in the ULM, especially in subduction zones, and their origins have been widely discussed (Courtier & Revenaugh, 2008; Schumacher & Thomas, 2016; Waszek et al., 2018). These detections are sensitive to the impedance contrasts across discontinuities and the most robust ones are at the depth of ~800 km and ~1000–1200 km, respectively. The dehydration of superhydrous phase B may account for the discontinuities at the depth of ~800 km in subduction zones (Z. Liu et al., 2016; Porritt & Yoshioka, 2016; D. Yang et al., 2017), but the ones at the depth of ~1000–1200 km were ascribed to various mechanisms, including viscosity jump (Marquardt & Miyagi, 2015; Rudolph et al., 2015), mineral phase transitions within subducted slab (King et al., 2015; Kingma et al., 1995), and the impedance contrasts between oceanic crust and other parts of a slab (Niu, 2014; Rost et al., 2008). Phase D, an important carrier of water to the ULM, is likely to dehydrate at a similar depth (Nishi et al., 2014), which could also contribute to some of these discontinuities.

Phase D is stable in the MTZ and the ULM in cold slabs. With increasing pressure and temperature, it would dehydrate into bridgmanite and stishovite, but it’s hard to constrain the transition depth due to its significantly large negative Clapeyron slope (Nishi et al., 2014). The dehydration temperature is around 1500 K and this decomposition may occur within a broad depth range of ~700–1200 km depending on the slab temperature (Nishi et al., 2014). $V_p$, $V_S$, and density contrasts between phase D and the aggregate of bridgmanite plus stishovite along a 1500 K isotherm are shown in Figure 7. It is expected that the velocity jumps caused by the dehydration of phase D decrease with increasing pressure since the velocities of phase D increase faster with pressure than those of bridgmanite and stishovite and the shear modulus of stishovite would soften at high pressures (R. Yang & Wu, 2014) (Figure 6). The velocity jumps caused by the dehydration of phase D are 6.6% for $V_p$ and 5.1% for $V_S$ at the depth of 660 km, but reduce to 2.3% and 0.3% at the depth of 1000 km, respectively (Figure 7). At deeper depths, the dehydration of phase D even results in a decrease in $V_S$. In contrast, the density jump caused by the dehydration of phase D is prominent with a value of ~15% at the depth of ~700–1200 km. The impedance contrasts ($\Delta(\rho V)$, where $\rho$ and $V$ represent the density and wave velocity, respectively) caused by the dehydration of phase D are 23% and 17% for compressional wave and of 22% and 15% for shear wave at the depth of 660 km and 1000 km, respectively, which are close to those caused by the transformation from olivine to wadsleyite (Núñez-Valdés et al., 2013). Such large impedance contrasts indicate that the dehydration of small amounts of phase D could produce seismically detectable discontinuities at the depth of ~1000–1200 km in subduction zones.

It should be noted that the effects of iron on the elasticity of phase D are not considered above. Previous studies indicate that the iron in Fe-Al-bearing phase D undergoes a high-spin to low-spin transition, which will significantly reduce the bulk modulus of phase D.
(Chang et al., 2013; X. Wu et al., 2016). The pressure range of the spin transition in Fe-Al-bearing phase D is related to the valence state of iron. The spin transition of Fe$^{2+}$ occurs at 37–41 GPa and the spin transition of Fe$^{3+}$ occurs at 40–65 GPa for $\sum\text{Fe}^{3+}/\text{Fe}=0.94$ and at 64–68 GPa for $\sum\text{Fe}^{3+}/\text{Fe}=0.40$ (Chang et al., 2013; X. Wu et al., 2016). Therefore, the spin transition of Fe$^{2+}$ in phase D and the dehydration of phase D are likely to occur simultaneously at the depth of $\sim$1000 km if phase D contains a certain amount of Fe$^{2+}$. The spin transition of Fe$^{2+}$ in phase D ($\text{Mg}_{0.89}\text{Fe}_{0.11}\text{Al}_{0.37}\text{Si}_{1.55}\text{H}_{2.65}\text{O}_{6}$, $\sum\text{Fe}^{2+}/\text{Fe}=0.60$) will cause a reduction of 28% on bulk sound velocity and a reduction of 1.7% on volume (X. Wu et al., 2016). Iron in bridgmanite occupies mainly in the Mg site as Fe$^{2+}$ or Fe$^{3+}$, and the iron does not experience any spin transition over the entire pressure range of the lower mantle. Si site in bridgmanite may contain a small amount of Fe$^{3+}$, and the Fe$^{3+}$ undergoes a spin transition at approximately 15–50 GPa (Lin et al., 2013), whose effect on bulk modulus of bridgmanite is relatively small at relevant mantle conditions (Badro, 2014; Cataldi et al., 2010, 2011; Shukla & Wentzcovitch, 2016). Therefore, the spin transition of Fe$^{2+}$ may significantly increase the $V_P$ jump and slightly decrease the density jump caused by the dehydration of phase D at the depth of $\sim$1000 km. Thus, the compressional impedance contrast caused by the dehydration of Fe-bearing phase D may significantly increase if the Fe$^{2+}$ in phase D undergoes a spin transition.

Seismic studies did detect some discontinuities at the depth of $\sim$700–1200 km, which may be related to the decomposition of phase D (Courtier & Revenaugh, 2008; Schumacher & Thomas, 2016; Waszek et al., 2018). Many discontinuities are roughly located within the fast anomalies in tomography models, that is, subducted slabs, where the dehydration of phase D occurs. The dehydration of phase D at the ULM primarily accounts for discontinuities with large impedance contrasts, specifically, density contrast. Therefore, seismic observations which are mainly sensitive to the velocity contrast, such as the S-to-P scatterers beneath the circum-Pacific regions at the depth of $\sim$1000–1200 km, may not result from the dehydration of phase D. The presence of oceanic crust could be a more convincing explanation (Kaneshima, 2019).

5 Conclusion

The elasticity of phase D at high pressures and high temperatures were investigated using first-principles calculations based on the density functional theory with the generalized gradient approximation. The thermodynamic and elastic properties agree well with the available experimental data. HBS is not found in our optimized structures and the bulk modulus of phase D doesn’t show an abrupt jump within the range of 30–40 GPa. Compared with other candidate minerals, the low-density feature of phase D could contribute to the stagnation of slabs at the ULM. In addition, phase D has larger pressure derivatives of $K$ and $G$ than those of major minerals in the MTZ and ULM, thus its velocities increase much faster with depth. As a result, unlike other hydrous phases, phase D exhibits higher velocities than ringwoodite at the MTZ and the $V_P$ and $V_S$ of phase D are only 0.5%–3.5% and 0%–2.0% lower than those of bridgmanite in the ULM, respectively. Therefore, the accumulation of phase D is not likely to cause obvious low-velocity anomalies in the ULM. In contrast, superhydrous phase B, another hydrous phase coexisting with phase D, may account for the low-velocity anomalies, whereas phase D could explain the shear wave splitting in the same region.

The velocity contrasts caused by the dehydration of phase D into stishovite and bridgmanite are not prominent at the ULM, but the impedance contrasts are significant because of the large density jump ($\sim$15%). The Fe$^{2+}$ in phase D will undergo spin transition at the depth around 1000 km, which significantly reduces the bulk modulus, further increasing the compressional impedance contrasts. Such large impedance contrasts may provide an alternative explanation for the discontinuities at the ULM in subduction regions.
The calculations in this study are based on the open-source quantum espresso package (https://www.quantum-espresso.org/) and the semianalytical method developed by Z. Wu and Wentzcovitch (2011). The data of phase D are shown in the Supporting Information for this article and are also available in the Zenodo database (https://doi.org/10.5281/zenodo.7503058). The data of other minerals are available in their respective intext citations.

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Figure 1. (a) The equation of states of phase D, (b) the relative change in volume \((V/V_0)\) and lattice constant \((a/a_0, c/c_0)\) as a function of pressure (this study: static results; experiments: data at 300 K). Solid lines represent our calculation results and the experimental results are shown with scatters. Chemical formulas: MgSi\(_2\)H\(_2\)O\(_6\) (this study), Mg\(_{1.11}\)Si\(_{1.89}\)H\(_{2.22}\)O\(_6\) (H. Yang et al., 1997), Mg\(_{1.14}\)Si\(_{1.7}\)H\(_{2.81}\)O\(_6\) (Ohtani et al., 1997), Mg\(_{1.11}\)Si\(_{1.8}\)H\(_{2.9}\)O\(_6\) (D. Frost & Fei, 1999), Mg\(_{0.92}\)Si\(_{1.7}\)H\(_{3.03}\)O\(_6\) (Shinmei et al., 2008), Mg\(_{1.0}\)Si\(_{1.7}\)H\(_{3.0}\)O\(_6\) (Hushur et al., 2011), Mg\(_{1.1}\)Si\(_{1.9}\)H\(_{2.4}\)O\(_6\) (Rosa et al., 2012), Mg\(_{1.1}\)Si\(_{1.8}\)H\(_{2.5}\)O\(_6\) (Rosa, Mezouar, et al., 2013; Rosa, Sanchez-Valle, et al., 2013), Mg\(_{1.14}\)Si\(_{1.7}\)H\(_{2.81}\)O\(_6\) (X. Wu et al., 2016), Mg\(_{0.89}\)Si\(_{1.3}\)Al\(_{0.64}\)H\(_{3.10}\)O\(_6\), Al-bearing phase D (Xu et al., 2020), Mg\(_{1.05}\)Si\(_{1.7}\)H\(_{3.05}\)O\(_6\) (Xu, Li, et al., 2021)
Figure 2. (a) thermal expansion, (b) thermal Grüneisen parameter, (c) heat capacity at constant volume, and (d) heat capacity at constant pressures of phase D. Solid lines represent our calculation results at various pressures and the black dashed line represents the experimental results at 0 GPa (Shinmei et al., 2008). Circles are thermal expansion at high pressures from HTBM EOS of phase D reported by Shinmei et al. (2008).

Figure 3. (a and b) elastic constants, (c) bulk modulus and shear modulus, (d) compressional wave velocity and shear wave velocity of phase D at various pressures and temperatures. Solid lines represent our calculation results and the experimental results are shown with scatters. Chemical formulas: This study, MgSi$_2$H$_2$O$_6$; Rosa12, Mg$_{1.1}$Si$_{1.9}$H$_{2.4}$O$_6$ (Rosa et al., 2012); Xu20+Al, Mg$_{0.89}$Si$_{1.30}$Al$_{0.64}$H$_{3.16}$O$_6$ (Xu et al., 2020); Xu21, Mg$_{1.03}$Si$_{1.71}$H$_{3.05}$O$_6$ (Xu, Li, et al., 2021).
Figure 4. The distances of the O-H bond and the O···H hydrogen bond of phase D at static conditions. The dots are placed at every 10 GPa from 0 GPa.
Figure 5. Anisotropy of phase D as a function of pressure. (a) $A_P$, (b) $A_S$, and (c) $A_{Po}$ of phase D at various pressures and temperatures. Red triangles represent the experimental results at ambient conditions obtained by Rosa et al. (2012)
Figure 6. (a) Compressional wave velocity $V_P$, (b) shear wave velocity $V_S$, and (c) densities of phase D compared to those of iron-free ringwoodite (Núñez-Valdez et al., 2013), stishovite (St) (R. Yang & Wu, 2014), iron-free bridgmanite (Pv) (Shukla et al., 2015) and periclase (Pc) (Z. Wu & Wentzcovitch, 2011) along a slab geotherm 500 K lower than the normal mantle geotherm (Brown & Shankland, 1981)
Figure 7. (a) Compressional wave velocity $V_P$, (b) shear wave velocity $V_S$, and (c) densities of phase D and the aggregate of bridgmanite (Pv) (Shukla et al., 2015) and stishovite (St) (R. Yang & Wu, 2014) along the 1500 K isotherm.
Figure 1.
This study compared with previous works (Yang97, Ohtani97, Frost99, Shinmei08, Hushur11, Rosa12, Rosa13a, Rosa13b, Wu16, Xu20+Al, Xu21). The unit-cell volume and length changes were examined at various temperatures (300 K, 700 K, 1100 K, 1500 K, 2000 K). The length and volume changes (a/a₀, c/c₀, v/v₀) were plotted against pressure (0-50 GPa). This study showed a consistent trend with previous experimental data, indicating reliability and accuracy.
Figure 2.
Figure 3.
Figure 4.
Figure 5.
Figure 6.
Figure 7.
Thermoelasticity of phase D and implications for low-velocity anomalies and local discontinuities at the uppermost lower mantle

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Key Points:

- Elasticity and density of phase D under the lower-mantle conditions are obtained using first-principles calculations
- Accumulation of phase D may account for seismic anisotropy rather than low-velocity anomalies in the uppermost lower mantle (ULM)
- Decomposition of phase D in the ULM causes a density jump, possibly explaining some discontinuities in subduction zones

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Abstract

Phase D is a potential water carrier in the slab subducted to the uppermost lower mantle (ULM) and its velocity and density characteristics are important for seismological detection of water cycle in the deep Earth. Here we obtained the density and velocities of phase D under the conditions of the ULM using first-principles calculations based on the density functional theory. In contrast to previous results, both hydrogen bond symmetrization and the corresponding abrupt increase in bulk modulus are absent in the optimized structure up to 80 GPa. The velocities of phase D are higher than those of periclase and only slightly lower than those of bridgmanite by 0.5%–3.5% for $V_P$ and by 0%–2.0% for $V_S$ in the ULM (660–1000 km), thus the accumulation of phase D can hardly produce obvious low-velocity anomaly in the ULM observed by seismological studies, but it may contribute significantly to the seismic anisotropy because of its strong elastic anisotropy.

Phase D will dehydrate into bridgmanite and stishovite at the depth of $\sim$700–1200 km. The velocity jumps are 6.6% for $V_P$ and 5.1% for $V_S$ at the depth of 660 km but reduce to 2.3% and 0.3% at the depth of 1000 km, respectively. However, phase D is $\sim$15% less dense than bridgmanite, so the dehydration of phase D could still produce large impedance jumps in the ULM, which may account for some discontinuities observed at the depth of $\sim$1000–1200 km in subduction zones.

Plain Language Summary

Water can be transported into the deep mantle through dense hydrous minerals by subduction slabs, some of which could be detected through geophysical observations because of their distinct physical properties, such as low seismic velocity and high electrical conductivity. Phase D is one of the important hydrous minerals in the uppermost lower mantle (ULM), but its elastic properties at the lower mantle conditions remain unclear. In this study, we obtain the elasticity and density of phase D under the conditions of the ULM. The velocities of phase D are comparable to those of major minerals in the ULM, so the enrichment of phase D is not likely to generate seismically detectable low-velocity anomaly, but the strong elastic anisotropy of phase D may explain some seismic anisotropy observations. Our results also show that the dehydration of phase D into bridgmanite and stishovite in the ULM produces negligible velocity contrasts but a prominent density increase, which could account for some seismic discontinuities with large density contrasts in the ULM.

1 Introduction

Water in the Earth’s interior exerts significant influences on the geochemical evolution and mantle dynamics because a small amount of water can significantly change the rheological properties, melting temperature, and diffusion rate of materials (Hirschmann, 2006; S.-i. Karato & Jung, 2003; Mei & Kohlstedt, 2000). There is significant amounts of evidence for the occurrence of water in the deep mantle. It has been shown that wadsleyite and ringwoodite, candidate nominally anhydrous minerals in the mantle transition zone (MTZ), could incorporate several weight percent of H$_2$O (Bell & Rossman, 1992; Inoue et al., 1995, 2010; Jacobsen et al., 2005; Smyth, 1987), whilst the hydrous ringwoodite and ice-VII discovered in superdeep diamonds (Pearson et al., 2014; Tschauner et al., 2018) provide direct evidence for the existence of the non-negligible amount of H$_2$O in the deep mantle. Water can be likely transported into the MTZ and the lower mantle via subducting slabs through the formation and dehydration of dense hydrous magnesium silicates (DHMSs) (Angel et al., 2001). Some geophysical anomalies, such as high $V_P/V_S$, high electrical conductivity, and low-velocity anomalies, were interpreted as locally high water content released by the dehydration of DHMSs (S.-i. Karato, 2011; J. Li et al., 2013; Savage, 2012) or merely their existence owing to their low-velocity characteristics (Z. Liu et al., 2016; Schmandt et al., 2014; D. Yang et al., 2017). Meanwhile, the generation/breakdown of DHMSs could cause considerable impedance contrasts, giving rise to seismic discontinuities. For example, the
decomposition of a small amount of superhydrous phase B could explain the 800-km discontinuity in western Pacific subduction zones (D. Yang et al., 2017), and the dehydration of phase H could produce significant seismic impedance increase in the mid-mantle (Song et al., 2022). Combining these seismological observations with the velocity and density characteristics, phase transitions, and corresponding impedance contrasts of DHMSs could help constrain the water content in the deep interior and provide insights into the circulation of water in the whole Earth.

Phase D is considered as a significant carrier of water in slabs subducted to the uppermost lower mantle (ULM). The ideal chemical formula of phase D is MgSi$_2$H$_2$O$_6$ containing 10 wt.% water, whereas the synthesized phase D shows a wide variation in Mg/Si from 0.53 to 0.71 and the water content varies from 10 wt.% to 18 wt.% (Chang et al., 2013; D. Frost & Fei, 1999; Hushur et al., 2011; Litasov et al., 2007; Rosa et al., 2012; Rosa, Mezouar, et al., 2013; Shinmei et al., 2008; X. Wu et al., 2016; Xu et al., 2020; Xu, Li, et al., 2021; H. Yang et al., 1997). Many hydrous phases exhibit low velocities (X. Li et al., 2016; Mao et al., 2012; Rosa et al., 2012, 2015; D. Yang et al., 2017) and could be identified by seismic observations. The weight fraction of phase D can be as high as 57% in hydrous peridotite (Ohtani et al., 2004), which is also possible to generate seismic velocity anomalies in the MTZ and the ULM. On the other hand, phase D will dehydrate into bridgmanite and stishovite at the temperature of around 1500 K and a wide depth range of $\sim$700–1200 km (Nishi et al., 2014). Correspondingly, many seismic studies have detected discontinuities exhibiting large impedance contrasts at the depth of $\sim$800–1200 km in subduction zones (Courtier & Revenaugh, 2008; Schumacher & Thomas, 2016; Waszek et al., 2018). There may exist a connection between these discontinuities and the dehydration of phase D, and the velocities and density of phase D under the lower mantle conditions are crucial for deciphering its role in such seismic observations.

The crystal structure and equation of state of phase D have been widely studied (D. J. Frost & Fei, 1998; D. Frost & Fei, 1999; Hushur et al., 2011; Kudoh et al., 1997; Litasov et al., 2007; L.-g. Liu, 1993; L.-G. Liu et al., 1998; Rosa et al., 2012; Rosa, Mezouar, et al., 2013; Shieh et al., 2009; Shinmei et al., 2008; X. Wu et al., 2016; Xue et al., 2008; H. Yang et al., 1997) and the elastic properties of Mg-endmember have also been investigated by first-principles calculations at static conditions (Mainprice et al., 2007; Tsuchiya & Tsuchiya, 2008) and Brillouin scattering and ultrasonic measurements at ambient conditions (L.-g. Liu et al., 2004; Rosa et al., 2012; Xu, Li, et al., 2021). The sound velocities of Al-bearing phase D up to 22 GPa and 1300 K were also determined by ultrasonic measurements (Xu et al., 2020). However, there are no elasticity data of Mg-phase D under both high-temperature and high-pressure conditions. In this contribution, we obtained the elastic properties of Mg-endmember phase D (MgSi$_2$H$_2$O$_6$) and its velocity and density characteristics under the lower mantle conditions using first-principles calculations within the generalized gradient approximation. Combining our results with available data of other minerals, we calculated the velocity and impedance contrasts caused by its dehydration and discussed its close relationship to seismic observations in the ULM.

### 2 Computational Detail

The ideal structure of phase D (MgSi$_2$H$_2$O$_6$) is trigonal with MgO$_6$ and SiO$_6$ octahedra in two separate layers stacked along the c-axis. The OH bonds of phase D are located between adjacent octahedra in the MgO$_6$ layer and the hydrogens are only 33% occupied (Xue et al., 2008; H. Yang et al., 1997). To maintain the symmetries of phase D, we constructed the same supercell as adopted in Mainprice et al. (2007) with edges $a$-$b$, $a$+2$b$, and $c$ to perform first-principles calculations and the space group is $P\overline{3}m1$.

All calculations in this study were performed based on the density functional theory (DFT) using the open-source quantum espresso package (Giannozzi et al., 2009) with the Generalized Gradient Approximation (GGA) (Hamann, 1997; Perdew et al., 1996).
energy cutoff for the plane wave was set to 70 Ry. Structural optimizations were performed using the variable cell-shape damped molecular dynamics method (Wentzcovitch et al., 1993) at certain pressures with a k-point mesh of 6×6×6, and the density functional perturbation theory (Baroni et al., 2001) was used to calculate the dynamical matrices with a 4×4×4 q-point mesh. The thermal elasticity of phase D was calculated using a semianalytical method developed by Z. Wu and Wentzcovitch (2011), similar to previous studies (Hao et al., 2019; Qian et al., 2018; Wang et al., 2019, 2021; Z. Wu & Wang, 2016; D. Yang et al., 2017; Yao et al., 2018; Zou et al., 2018).

3 Results

3.1 Thermodynamic Properties

The calculated equations of state of phase D are shown together with the experimental measurements in Figure 1a. The differences among experiments primarily result from the wide variations in Mg/Si ratio, aluminum content, and water content in the synthesized phase D. Except the Al-bearing phase D (Xu et al., 2020), most measured volumes (D. Frost & Fei, 1999; Hushur et al., 2011; Ohtani et al., 2004; Rosa et al., 2012; Rosa, Mezouar, et al., 2013; Rosa, Sanchez-Valle, et al., 2013; Shinmei et al., 2008; X. Wu et al., 2016; Xu, Li, et al., 2021; H. Yang et al., 1997) are slightly smaller than our calculated results due to the overestimation of GGA calculation, but there is much better consistency in the relative change of volume \( V/V_0 \) with pressure (Figure 1b). Our calculated results lie between the experimental data of Shinmei et al. (2008) and X. Wu et al. (2016) within a broad pressure range (Figure 1b) and agree with those of Rosa, Mezouar, et al. (2013) at all pressures (Figure 1b). Furthermore, the calculated relative changes in cell parameters are also consistent with the experimental results. In comparison with the absolute values at different pressures, the relative changes in volume \( V/V_0 \) and lattice constants (a/a_0, c/c_0) play a more important role in the determination of the compressional properties.

The calculated thermal expansion \( \alpha = \frac{1}{V} \frac{\partial V}{\partial T} \) of phase D as well as the experimental data (Shinmei et al., 2008) are shown in Figure 2a. The black dashed line represents the experimental results at 0 GPa (Shinmei et al., 2008), which are larger than our calculated results. The thermal expansion of Shinmei et al. (2008) was calculated using the high-temperature Birch-Murnaghan equation of state (HTBM EOS) based on the P-V-T data of phase D. It should be noted that there are only two room-temperature volume data points at ambient pressure in their study, whereas most of the data were measured at 17–46 GPa. Therefore, their thermal expansion of phase D at high pressures should be more convincing than that at 0 GPa. As shown in Figure 2a, these high-pressure data agree better with our calculated results. The calculated thermal Gruneisen parameter, heat capacity at constant volume \( CV \) and constant pressure \( CP \) are also shown in Figure 2.

3.2 Thermal Elastic Properties

The elastic tensor of phase D with a trigonal symmetry can be totally determined by six independent elastic constants \( \{C_{11}, C_{33}, C_{12}, C_{13}, C_{44}, C_{14}\} \). The calculated thermal elastic constants, adiabatic bulk \( K_S \) and shear \( G \) moduli, longitudinal \( V_P \) and shear wave \( V_S \) velocities, as well as the experimental data (Rosa et al., 2012; Xu et al., 2020; Xu, Li, et al., 2021), are shown in Figure 3. The first and second derivatives of elastic moduli \( M = C_{ij} \), \( K_S \), and \( G \) with respect to pressure and temperature are shown in Table S1 and Table S2, respectively. The calculated compressional elastic constants \( \{C_{11} \) and \( C_{33}\) and shear elastic constant \( C_{44}\) are slightly larger than the experimental results (Rosa et al., 2012), whereas the off-diagonal elastic constants \( \{C_{12}, C_{13}, \) and \( C_{14}\)\) are a little smaller (Figure 3a and 3b). Since there are no high-pressure experimental data of the elastic constants of phase D, we compared the linear compressibility calculated from our elastic constants with that from the lattice constants of experimental data and they exhibit good consistency (Text S1; Figure S1).
The adiabatic bulk moduli ($K_S$) are in good agreement with the experimental results of Rosa et al. (2012) and slightly larger than that of Xu et al. (2020) and Xu, Li, et al. (2021), but our shear moduli ($G$) are significantly larger than all experiments, especially Xu, Li, et al. (2021) (Figure 3c). The deviations probably result from different Al and H$_2$O contents in phase D. Phase D in this study contains 10 wt.% H$_2$O, whereas the synthesized samples in Rosa et al. (2012) and Xu, Li, et al. (2021) include 12.1 and 16.1 wt.% H$_2$O, respectively, and the sample in Xu et al. (2020) contains both 18.8 wt.% Al$_2$O$_3$ and ~16.0 wt.% H$_2$O. The negative correlation between H$_2$O content and elastic moduli is consistent with many minerals, such as wadsleyite and ringwoodite (Wang et al., 2019, 2021), but the effect of aluminum content on the elastic moduli of phase D requires further investigation. Since the density of phase D in this study is close to these experiments and the compressional and shear wave velocities are expressed by $V_P = \sqrt{(K_S + \frac{4}{3}G)/\rho}$ and $V_S = \sqrt{G/\rho}$, the larger shear moduli in our results further lead to higher velocities (Figure 3d). The $V_P$ and $V_S$ of phase D in this study are 2.9% and 5.7% larger than that in Rosa et al. (2012) at ambient conditions and approximately 4–6% and 8–9% larger than that in Xu, Li, et al. (2021) at pressures of 3–13.6 GPa, respectively, exhibiting the significant effect of various water contents.

Previous theoretical studies (Tsuchiya et al., 2005; Tsuchiya & Tsuchiya, 2008) suggested that the hydrogen bond symmetrization (HBS) (the H atom is located at the middle point of two neighboring O atoms) would occur in phase D at 40 GPa, causing a ~20% increase in the bulk modulus. However, HBS is absent in our optimized structures up to 80 GPa (Figure 4) and such an increase in the bulk modulus is not observed in this study and Mainprice et al. (2007). The discrepancy may be caused by different structure models of phase D. The structure in Tsuchiya et al. (2005) is distorted from trigonal symmetry and has a triclinic unit cell due to the fractional occupancy of hydrogen. To solve this problem, Mainprice et al. (2007) constructed a corresponding supercell with the space group $P\overline{3}m1$ (adopted in this study) instead of $P\overline{3}1m$. Despite this discrepancy, infrared spectroscopic studies on phase D observe neither significant changes in the frequency or intensity of OH stretching vibrations nor the merging of the separate OH peaks with increasing pressure up to 42 GPa (Shieh et al., 2009). Moreover, no direct experimental results hitherto indicate that the bulk modulus of phase D will increase abruptly around 40 GPa. The dramatic increase in bulk modulus observed by Hushur et al. (2011) probably results from the assumption that $K'_0$ (the pressure derivative of the bulk modulus at 0 GPa) is 4, whereas both Rosa et al. (2012) and this study obtain a value close to 5, significantly larger than their estimate and that of major minerals in the MTZ and lower mantle.

### 3.3 Anisotropy

The elastic wave velocities of single crystal usually exhibit variations along different crystallographic orientations and the single-crystal anisotropy can be defined as in Karki et al. (2001):

\[
A_P = 2 \times \frac{V_{P,max} - V_{P,min}}{V_{P,max} + V_{P,min}} \\
A_S = 2 \times \frac{V_{S,max} - V_{S,min}}{V_{S,max} + V_{S,min}} \\
A_{P0} = 2 \times \frac{(V_{S1} - V_{S2})_{max}}{V_{S1} + V_{S2}}
\]

where $A_P$, $A_S$ and $A_{P0}$ represent the $V_P$, $V_S$, and $V_S$ polarization anisotropies, respectively. $V_P$, $V_{S1}$, and $V_{S2}$ represent the wave velocities along a given crystallographic orientation, which can be calculated using the Christoffel equation (Musgrave, 1970):
Here $C_{ijkl}$ refers to the fourth-ranked elastic tensor and the unit vector $n = (n_1, n_2, n_3)$ is the propagation direction of the elastic wave. $V$ and $\rho$ represent velocity and density, respectively.

The $V_S$ wave polarization anisotropy of phase D is significantly large (approximately 18%) in the MTZ and the ULM (Figure 5). Rosa, Sanchez-Valle, et al. (2013) indicate that phase D exhibits a relatively low strength under uniaxial compression and tends to develop lattice preferred orientations under plastic flow. They also estimated that 16 vol.% of phase D in hydrous subducted peridotite could explain the shear wave splitting (0.9±0.3%) and the shear wave ray polarization geometry observed in a detached fragment of the Tonga slab below the MTZ (Chen & Brudzinski, 2003). Our calculated anisotropies of phase D are similar to those in Rosa et al. (2012) (Figure 5), further corroborating this interpretation.

4 Discussions

4.1 The Velocities and Density Characteristics of Phase D in the MTZ and ULM

The seismic velocities and density of phase D, ringwoodite, periclase, bridgmanite, and stishovite along a cold geotherm are shown in Figure 6. Similar to other hydrous phases, phase D shows an obvious low-density feature, especially at the ULM, and the density contrast between phase D and bridgmanite is up to 15%, thus its presence could contribute to the stagnation of slabs at the depth of ~600–1000 km (Fukao et al., 2009) to a large extent. The velocity characteristics, however, are quite different. Unlike other hydrous phases, phase D shows relatively high wave velocities in the MTZ, and the velocities of phase D increase much faster with pressure than those of candidate minerals in the MTZ and ULM (Figure 6) due to its large pressure derivatives of $K_S$ and $G$ (Table S1). Its $V_P$ and $V_S$ are 1.5%–3.0% and 6.8%–9.1% higher than those of ringwoodite at depths of ~500–660 km, respectively. Stishovite, one of the dehydration products of phase D (Nishi et al., 2014) and an important component in the oceanic crust, has significantly high velocities in the MTZ. The velocity contrasts between phase D and stishovite are 14.1%–18.6% for $V_P$ and 10.8%–13.5% for $V_S$ in the MTZ. However, due to the softening of the shear modulus of stishovite (Karki et al., 1997; R. Yang & Wu, 2014) and the large pressure dependence of velocities of phase D, the $V_P$ and $V_S$ of stishovite are only 5.6% and 1.6% higher than those of phase D at the depth of 1000 km, respectively, which become even smaller at larger depths. Similarly, although phase D exhibits much lower velocities than bridgmanite at ambient conditions as in Rosa et al. (2012), the velocity contrasts between phase D and bridgmanite are not prominent for both $V_P$ (~0.5%–3.5%) and $V_S$ (~0%–2%) within the depth range of ~660–1000 km (Figure 6). This indicates that the accumulation of phase D can hardly produce an obvious low-velocity anomaly in the ULM observed in seismological studies (Brudzinski & Chen, 2003; Z. Liu et al., 2016), which is inconsistent with the conclusion at ambient conditions (Rosa et al., 2012). However, as mentioned above, the velocities of phase D are negatively correlated with the H$_2$O content, so a higher H$_2$O content may increase the possibility of generating low-velocity anomalies, but it still requires more quantitative investigations on the effect. Xu et al. (2020) used the data of Al-bearing phase D, which include 18.8 wt% Al$_2$O$_3$ and ~16.0 wt% H$_2$O, to calculate the velocities and density contrasts between the dry and hydrous harzburgite, indicating that the hydrous harzburgite with ~1.2 wt.% H$_2$O only exhibits slightly lower velocities at the ULM, ~0.5% and ~1.0% for $V_P$ and $V_S$ respectively, hardly accounting for the ~3% velocity anomalies for both $V_P$ and $V_S$ in Tonga slab (Brudzinski & Chen, 2003), although the Al-bearing phase D has lower velocities than ours under such conditions (Figure 3d). This could provide an approximate estimation on the H$_2$O effect, that is, such a water content is not enough to cause obvious low-velocity anomalies, but the contribution of Al to the velocities remains to be explored.
In contrast, superhydrous phase B, another stable hydrous mineral in cold slabs in the ULM, may account for low-velocity observations. It has much lower velocities than bridgmanite and periclase, and the released water by its dehydration at the depth of ~800 km should migrate upwards, causing the partial melt to reduce the velocity at a shallower depth (D. Yang et al., 2017). However, superhydrous phase B has negligible anisotropy compared with phase D under such conditions, which cannot explain the observed seismic anisotropy in the same region (Chen & Brudzinski, 2003). Therefore, the low-velocity anomaly could be mainly caused by superhydrous phase B, whereas the presence of phase D could primarily account for the seismic anisotropy. In addition, it has been found that phase D and superhydrous phase B are likely to coexist in the ULM (Nishi et al., 2014; Xu, Inoue, et al., 2021), further supporting both observations in the same region.

### 4.2 The Dehydration of Phase D and Implications on Discontinuities in the ULM

Besides the global 410-km and 660-km discontinuities, seismological studies detected many local discontinuities in the ULM, especially in subduction zones, and their origins have been widely discussed (Courtier & Revenaugh, 2008; Schumacher & Thomas, 2016; Waszek et al., 2018). These detections are sensitive to the impedance contrasts across discontinuities and the most robust ones are at the depth of ~800 km and ~1000–1200 km, respectively. The dehydration of superhydrous phase B may account for the discontinuities at the depth of ~800 km in subduction zones (Z. Liu et al., 2016; Porritt & Yoshioka, 2016; D. Yang et al., 2017), but the ones at the depth of ~1000–1200 km were ascribed to various mechanisms, including viscosity jump (Marquardt & Miyagi, 2015; Rudolph et al., 2015), mineral phase transitions within subducted slab (King et al., 2015; Kingma et al., 1995), and the impedance contrasts between oceanic crust and other parts of a slab (Niu, 2014; Rost et al., 2008). Phase D, an important carrier of water to the ULM, is likely to dehydrate at a similar depth (Nishi et al., 2014), which could also contribute to some of these discontinuities.

Phase D is stable in the MTZ and the ULM in cold slabs. With increasing pressure and temperature, it would dehydrate into bridgmanite and stishovite, but it’s hard to constrain the transition depth due to its significantly large negative Clapeyron slope (Nishi et al., 2014). The dehydration temperature is around 1500 K and this decomposition may occur within a broad depth range of ~700–1200 km depending on the slab temperature (Nishi et al., 2014). \( V_P, V_S \), and density contrasts between phase D and the aggregate of bridgmanite plus stishovite along a 1500 K isotherm are shown in Figure 7. It is expected that the velocity jumps caused by the dehydration of phase D decrease with increasing pressure since the velocities of phase D increase faster with pressure than those of bridgmanite and stishovite and the shear modulus of stishovite would soften at high pressures (R. Yang & Wu, 2014) (Figure 6). The velocity jumps caused by the dehydration of phase D are 6.6% for \( V_P \) and 5.1% for \( V_S \) at the depth of 660 km, but reduce to 2.3% and 0.3% at the depth of 1000 km, respectively (Figure 7). At deeper depths, the dehydration of phase D even results in a decrease in \( V_S \). In contrast, the density jump caused by the dehydration of phase D is prominent with a value of ~15% at the depth of ~700–1200 km. The impedance contrasts (\( \Delta (\rho V) \), where \( \rho \) and \( V \) represent the density and wave velocity, respectively) caused by the dehydration of phase D are 23% and 17% for compressional wave and of 22% and 15% for shear wave at the depth of 660 km and 1000 km, respectively, which are close to those caused by the transformation from olivine to wadsleyite (Núñez-Valdez et al., 2013). Such large impedance contrasts indicate that the dehydration of small amounts of phase D could produce seismically detectable discontinuities at the depth of ~1000–1200 km in subduction zones.

It should be noted that the effects of iron on the elasticity of phase D are not considered above. Previous studies indicate that the iron in Fe-Al-bearing phase D undergoes a high-spin to low-spin transition, which will significantly reduce the bulk modulus of phase D.
The pressure range of the spin transition in Fe-Al-bearing phase D is related to the valence state of iron. The spin transition of Fe$^{2+}$ occurs at 37–41 GPa and the spin transition of Fe$^{3+}$ occurs at 40–65 GPa for $\sum$Fe$^{3+}$/Fe = 0.94 and at 64–68 GPa for $\sum$Fe$^{3+}$/Fe= 0.40 (Chang et al., 2013; X. Wu et al., 2016). Therefore, the spin transition of Fe$^{2+}$ in phase D and the dehydration of phase D are likely to occur simultaneously at the depth of ~1000 km if phase D contains a certain amount of Fe$^{2+}$. The spin transition of Fe$^{2+}$ in phase D ($\text{Mg}_{0.89}\text{Fe}_{0.11}\text{Al}_{0.37}\text{Si}_{1.55}\text{H}_{2.65}\text{O}_{6}$, $\sum$Fe$^{2+}$/Fe=0.60) will cause a reduction of 28% on bulk sound velocity and a reduction of 1.7% on volume (X. Wu et al., 2016). Iron in bridgmanite occupies mainly in the Mg site as Fe$^{2+}$ or Fe$^{3+}$, and the iron does not experience any spin transition over the entire pressure range of the lower mantle. Si site in bridgmanite may contain a small amount of Fe$^{3+}$, and the Fe$^{3+}$ undergoes a spin transition at approximately 15–50 GPa (Lin et al., 2013), whose effect on bulk modulus of bridgmanite is relatively small at relevant mantle conditions (Badro, 2014; Catali et al., 2010, 2011; Shukla & Wentzcovitch, 2016). Therefore, the spin transition of Fe$^{2+}$ may significantly increase the $V_P$ jump and slightly decrease the density jump caused by the dehydration of phase D at the depth of ~1000 km. Thus, the compressional impedance contrast caused by the dehydration of Fe-bearing phase D may significantly increase if the Fe$^{2+}$ in phase D undergoes a spin transition.

Seismic studies did detect some discontinuities at the depth of ~700–1200 km, which may be related to the decomposition of phase D (Courtier & Revenaugh, 2008; Schumacher & Thomas, 2016; Waszek et al., 2018). Many discontinuities are roughly located within the fast anomalies in tomography models, that is, subducted slabs, where the dehydration of phase D occurs. The dehydration of phase D at the ULM primarily accounts for discontinuities with large impedance contrasts, specifically, density contrast. Therefore, seismic observations which are mainly sensitive to the velocity contrast, such as the S-to-P scatterers beneath the circum-Pacific regions at the depth of ~1000–1200 km, may not result from the dehydration of phase D. The presence of oceanic crust could be a more convincing explanation (Kaneshima, 2019).

5 Conclusion

The elasticity of phase D at high pressures and high temperatures were investigated using first-principles calculations based on the density functional theory with the generalized gradient approximation. The thermodynamic and elastic properties agree well with the available experimental data. HBS is not found in our optimized structures and the bulk modulus of phase D doesn’t show an abrupt jump within the range of 30–40 GPa. Compared with other candidate minerals, the low-density feature of phase D could contribute to the stagnation of slabs at the ULM. In addition, phase D has larger pressure derivatives of $K$ and $G$ than those of major minerals in the MTZ and ULM, thus its velocities increase much faster with depth. As a result, unlike other hydrous phases, phase D exhibits higher velocities than ringwoodite at the MTZ and the $V_P$ and $V_S$ of phase D are only 0.5%–3.5% and 0%–2.0% lower than those of bridgmanite in the ULM, respectively. Therefore, the accumulation of phase D is not likely to cause obvious low-velocity anomalies in the ULM. In contrast, superhydrous phase B, another hydrous phase coexisting with phase D, may account for the low-velocity anomalies, whereas phase D could explain the shear wave splitting in the same region.

The velocity contrasts caused by the dehydration of phase D into stishovite and bridgmanite are not prominent at the ULM, but the impedance contrasts are significant because of the large density jump (~15%). The Fe$^{2+}$ in phase D will undergo spin transition at the depth around 1000 km, which significantly reduces the bulk modulus, further increasing the compressional impedance contrasts. Such large impedance contrasts may provide an alternative explanation for the discontinuities at the ULM in subduction regions.
6 Open Research

The calculations in this study are based on the open-source quantum espresso package (https://www.quantum-espresso.org/) and the semianalytical method developed by Z. Wu and Wentzcovitch (2011). The data of phase D are shown in the Supporting Information for this article and are also available in the Zenodo database (https://doi.org/10.5281/zenodo.7503058). The data of other minerals are available in their respective intext citations.

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Figure 1. (a) The equation of states of phase D, (b) the relative change in volume ($V/V_0$) and lattice constant ($a/a_0$, $c/c_0$) as a function of pressure (this study: static results; experiments: data at 300 K). Solid lines represent our calculation results and the experimental results are shown with scatters. Chemical formulas: MgSi$_2$H$_2$O$_6$ (this study), Mg$_{1.11}$Si$_{1.89}$H$_{2.22}$O$_6$ (H. Yang et al., 1997), Mg$_{1.14}$Si$_{1.73}$H$_{2.81}$O$_6$ (Ohtani et al., 1997), Mg$_{1.11}$Si$_{1.6}$H$_{3.6}$O$_6$ (D. Frost & Fei, 1999), Mg$_{1.02}$Si$_{1.74}$H$_{3.05}$O$_6$ (Shinmei et al., 2008), Mg$_{1.0}$Si$_{1.7}$H$_{3.0}$O$_6$ (Hushur et al., 2011), Mg$_{1.1}$Si$_{1.9}$H$_{2.4}$O$_6$ (Rosa et al., 2012), Mg$_{1.1}$Si$_{1.8}$H$_{2.2}$O$_6$ (Rosa, Mezouar, et al., 2013; Rosa, Sanchez-Valle, et al., 2013), Mg$_{1.14}$Si$_{1.73}$H$_{2.81}$O$_6$ (X. Wu et al., 2016), Mg$_{0.89}$Si$_{1.30}$Al$_{0.64}$H$_{3.10}$O$_6$, Al-bearing phase D (Xu et al., 2020), Mg$_{1.0}$Si$_{1.71}$H$_{4.05}$O$_6$ (Xu, Li, et al., 2021)
Figure 2. (a) thermal expansion, (b) thermal Grüneisen parameter, (c) heat capacity at constant volume, and (d) heat capacity at constant pressures of phase D. Solid lines represent our calculation results at various pressures and the black dashed line represents the experimental results at 0 GPa (Shinmei et al., 2008). Circles are thermal expansion at high pressures from HTBM EOS of phase D reported by Shinmei et al. (2008).

Figure 3. (a and b) elastic constants, (c) bulk modulus and shear modulus, (d) compressional wave velocity and shear wave velocity of phase D at various pressures and temperatures. Solid lines represent our calculation results and the experimental results are shown with scatters. Chemical formulas: This study, MgSi$_2$H$_2$O$_6$; Rosa12, Mg$_{1.1}$Si$_{1.9}$H$_{2.4}$O$_6$ (Rosa et al., 2012); Xu20+Al, Mg$_{50.89}$Si$_{1.30}$Al$_{0.64}$H$_{3.10}$O$_6$ (Xu et al., 2020); Xu21, Mg$_{1.03}$Si$_{1.71}$H$_{3.05}$O$_6$ (Xu, Li, et al., 2021).
Figure 4. The distances of the O-H bond and the O···H hydrogen bond of phase D at static conditions. The dots are placed at every 10 GPa from 0 GPa.
Figure 5. Anisotropy of phase D as a function of pressure. (a) $A_P$, (b) $A_S$, and (c) $A_{Po}^S$ of phase D at various pressures and temperatures. Red triangles represent the experimental results at ambient conditions obtained by Rosa et al. (2012)
Figure 6. (a) Compressional wave velocity $V_p$, (b) shear wave velocity $V_s$, and (c) densities of phase D compared to those of iron-free ringwoodite (Núñez-Valdez et al., 2013), stishovite (St) (R. Yang & Wu, 2014), iron-free bridgmanite (Pv) (Shukla et al., 2015) and periclase (Pc) (Z. Wu & Wentzcovitch, 2011) along a slab geotherm 500 K lower than the normal mantle geotherm (Brown & Shankland, 1981)
Figure 7. (a) Compressional wave velocity $V_P$, (b) shear wave velocity $V_S$, and (c) densities of phase D and the aggregate of bridgmanite (Pv) (Shukla et al., 2015) and stishovite (St) (R. Yang & Wu, 2014) along the 1500 K isotherm.