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Hydrogen-Bond Symmetrization of δ-AlOOH *

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The δ-AlOOH can transport water into the deep mantle along cold subducting slab geotherm. We investigate the hydrogen-bond symmetrization behavior of δ-AlOOH under the relevant pressure-temperature condition of the lower mantle using ab initio molecular dynamics (MD). The static symmetrization pressure of 30.0 GPa can be reduced to 17.0 GPa at 300 K by finite-temperature (T) statistics, closer to the experimental observation of ∼10.0 GPa. The symmetrization pressure obtained by MD simulation is related to T by $P\,(\mathrm{GPa}) = 13.9\,(\mathrm{GPa}) + 0.01\,(\mathrm{GPa/K}) \times T\,(\mathrm{K})$. *We conclude that δ-AlOOH in the lower mantle exists with symmetric hydrogen bond from its birthplace, or someplace slightly deeper, to the core-mantle boundary (CMB) along cold subducting slab geotherm. The bulk modulus decreases with T and increases anomalously upon symmetrization:* $K_0\,(\mathrm{GPa}) = 181\,(\mathrm{GPa}) - 0.013\,(\mathrm{GPa/K}) \times T\,(\mathrm{K})$ *for δ-AlOOH with asymmetric hydrogen bond, and* $K_0\,(\mathrm{GPa}) = 216\,(\mathrm{GPa}) - 0.013\,(\mathrm{GPa/K}) \times T\,(\mathrm{K})$ *for δ-AlOOH with symmetric hydrogen bond. Our results provide an important insight into the existent form and properties of δ-AlOOH in the lower mantle.*

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Water plays an important role in the evolution of Earth because it changes the physical properties of mantle materials, including the melting temperature, viscosity, and diffusion rate.[1] Most of the hydrous phases, such as the superhydrous phase B, phase D and phase E, decompose and dehydrate above the deep lower mantle due to the high temperature.[1] However, phase δ (δ-AlOOH), phase H ($MgSiO_4H_2$) and their solid solution (δ-AlOOH-$MgSiO_4H_2$) can be stable down to the CMB below subduction zone.[2–4] The properties of δ-AlOOH under conditions of high temperature and high pressure can inform discussions of the water content and distribution in the lower mantle.

The hydroxyl group (OH) in hydrous phases is weakly attracted to a neighboring oxygen atom on the opposite site, presenting an asymmetric O-H···O configuration under ambient conditions,[5] where the potential surface along the two neighboring atoms is double-well and the hydrogen atom is bound to one neighboring oxygen atom. With the increasing pressure, the potential barrier between the two neighboring atoms becomes so low that the H atoms' zero-point energy can wash it out. In this case, H atoms distribute broadly and flatly in a unimodal centering at the midpoint between the two nearest O atoms, and the hydrogen bond presents a symmetric configuration. When pressure increases further, the potential surface may finally change to a single well, with the hydrogen atom centered perfectly between its two neighboring atoms.[6–8] This process, defined as pressure-induced hydrogen-bond symmetrization, has been described by both experiments and first-principles calculations for ice,[9,10] α-FeOOH,[11] ε-FeOOH[12] and δ-AlOOH.[13–15] Hydrogen-bond symmetrization produces significant effects on the properties of the hosts, such as an increase in elasticity.[5,16] Additionally, hydrogen-bond symmetrization is coupled with the spin transition of Fe^{3+}, i.e., the hydrogen-bond symmetrization can assist in ferric spin collapse. In turn, the ferric spin collapse would accelerate the symmetrization in the case of FeOOH.[11,12]

The δ-AlOOH, formed at the top of the lower mantle from the decomposition of phase Egg,[17] is the high-pressure polymorph of α- and γ-AlOOH.[13] The properties of δ-AlOOH have been examined and discussed by several groups.[13–15] Some experimental evidence, such as the abnormalities observed in the shift of vibrational peaks and the change of axial compressibility under high pressure, indicates that δ-AlOOH undergoes an asymmetric-to-symmetric transition of hydrogen bonds at approximately 10.0 GPa and at room temperature. However, this critical pressure for the hydrogen-bond symmetrization of δ-AlOOH is calculated by first principles to be approximately 30.0 GPa.[13,16,18] Thus a considerable gap of 20.0 GPa exists compared with the experimentally measured values. The most likely reason for this discrepancy is that previous calculations were based on static calculations and did not take into account the thermal vibration effects and quantum effects, which can affect the symmetrization pressure. Molecular dynamics simulation is a successful method to take into account of thermal vibration effects, and has been widely ap-

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plied to the investigations of many materials.[19–23] Bronstein *et al.*[24] have recently performed standard MD simulations taking account of thermal vibrational effects and quantum thermal bath (QTB) MD taking account of thermal vibrational and nuclear quantum effects on δ-AlOOH at 300 K. Here we performed a series of standard MD simulations for δ-AlOOH at high pressures and 300, 1000, 1500 and 2000 K. To our knowledge, this is the first high-temperature MD report on δ-AlOOH. We have obtained the relationship between the symmetrization pressure of δ-AlOOH and temperature.

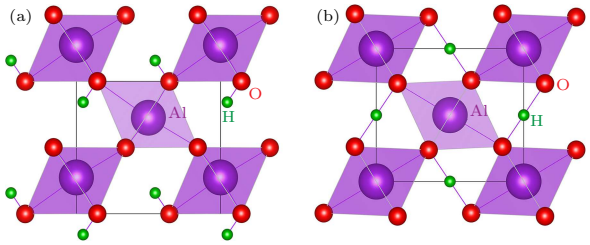


Fig. 1. Crystal structures of δ-AlOOH. (a) The hydrogen bond is asymmetric. (b) The hydrogen bond is symmetric.

Our simulations were performed using the plane wave-based density-functional theory (DFT) code Vienna ab-initio simulation package (VASP).[25,26] Projector-augmented wave potentials along with a 750 eV plane-wave cut-off energy were employed in both static calculations and standard MD calculations. In the static calculations, an 8-atom unit cell was calculated with the Perdew–Burke–Ernzerhof (PBE) exchange-correlation function[27] using a (5 × 5 × 8) Monkhorst–Pack grid to sample the Brillouin zone. Two structure candidates were employed, i.e., the structure with asymmetric hydrogen bond, possessing the $P2_1nm$ space group, and the structure with symmetric hydrogen bond, possessing the $Pnnm$ space group (Fig. 1, Table S1). Higher cut-off energies and denser Monkhorst–Pack grids have slight significance. Based on the optimized structures from static calculations, supercells containing 64 atoms were adopted in the MD calculations, in which we used a (2 × 2 × 4) Monkhorst–Pack grid. We performed isothermal–isobaric molecular dynamics (NPT-MD) (constant pressure and temperature) simulations at 300, 1000, 1500 and 2000 K. All of the pressures used in the present study are real statistical pressures. Each MD simulation at a finite temperature and pressure was run for 11000 steps using a step of 1 fs, and the final 10000 steps (10 ps) were included in the analysis.

Under the 0 GPa and 0 K condition, R_{O-H} is 1.040 Å and $R_{O\cdots H}$ is 1.510 Å, presenting an asymmetric hydrogen bond. With increasing pressure, R_{O-H} increases while $R_{O\cdots H}$ decreases almost linearly (Fig. 2(a)). At 25.0 GPa, the hydrogen bond is still asymmetric (1.159 Å for R_{O-H} and 1.223 Å for $R_{O\cdots H}$). However, at 30.0 GPa, R_{O-H} and $R_{O\cdots H}$ reach almost the same length, with a difference of 0.001 Å, and R_{O-H} becomes $1/2R_{OO}$ (the nearest neighboring O···O distance), indicating that the hydrogen atom is located at the center between the two oxygen atoms (the inset of Fig. 2(a)). Thus we propose that δ-AlOOH undergoes an asymmetric-to-symmetric transition of the hydrogen bond at 30.0 GPa and 0 K, in agreement with the previous results.[16,18] Figure 2(b) shows that the a/c and b/c ratios of δ-AlOOH with asymmetric hydrogen bond decrease below 25.0 GPa and increase above 25.0 GPa, in agreement with those observed experimentally (Fig. 2(b)),[14] except for the critical pressures (expt. ∼10.0 GPa; theor. ∼30.0 GPa). Placed on the plane composed of the a and b axes, the asymmetric hydrogen bond is easily compressed, while the symmetric bond is difficult to compress due to its increased strength.[28] As a result, the a and b axes are more compressible than the c axis in δ-AlOOH with asymmetric hydrogen bond but less compressible in δ-AlOOH with symmetric hydrogen bond.

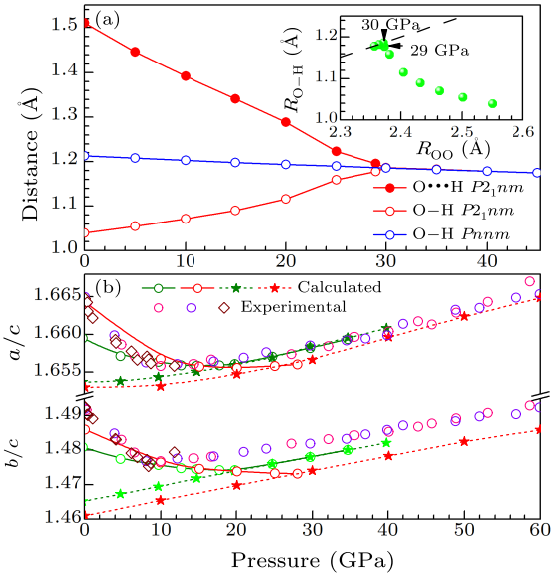


Fig. 2. (a) O-H and O···H distances in δ-AlOOH at different pressures calculated at 0 K. The evolution of R_{O-H} as a function of R_{OO} is displayed as an inset in this figure. The dots are placed every 5.0 GPa from 0 GPa, except for the 29.0 GPa point. The dashed line has the relationship of $R_{O-H} = 1/2R_{OO}$, indicating the symmetrization. (b) The a/c and b/c ratios versus pressure in δ-AlOOH. The green solid and green dashed lines, respectively, represent the results of δ-AlOOH with asymmetric hydrogen bond and δ-AlOOH with symmetric hydrogen bond in the present study. The red solid and red dashed lines indicate the theoretical results in the literature.[16] The magenta and purple open circles represent the experimental results by Sano-Furukawa *et al.*[14] and the wine open diamonds represent the experimental results by Kuribayashi *et al.*[29]

To understand in detail the evolution of the hydrogen atom probability distribution (P) at high-pressure and high-temperature, we plot it as a function of the hydrogen-atom transfer coordinate along the hydrogen bond (δ) and the corresponding O···O distance (R_{OO}) at different pressures and temperatures in Fig. 3, and the additional figures are shown in Fig. S1 in supplementary materials. The parameter δ is defined for each hydrogen atom as its transfer coordinate along the hydrogen bond. This coordinate is the difference between the distances of this hydro-

gen atom to the two oxygen atoms at the ends of this hydrogen bond. When the coordinate is zero, the hydrogen is shared by two oxygen atoms and remains in the center of the hydrogen bond. When the coordinate is large in magnitude on both the positive and negative sides, the hydrogen is bound to one oxygen atom. Asymmetric structures are reflected by the double-peak distributions, indicative of larger probabilities that hydrogen atoms will stay away from the center, whereas single-peak distributions represent symmetric structures, in which hydrogen atoms are located at the center of the two nearest oxygen atoms.[30]

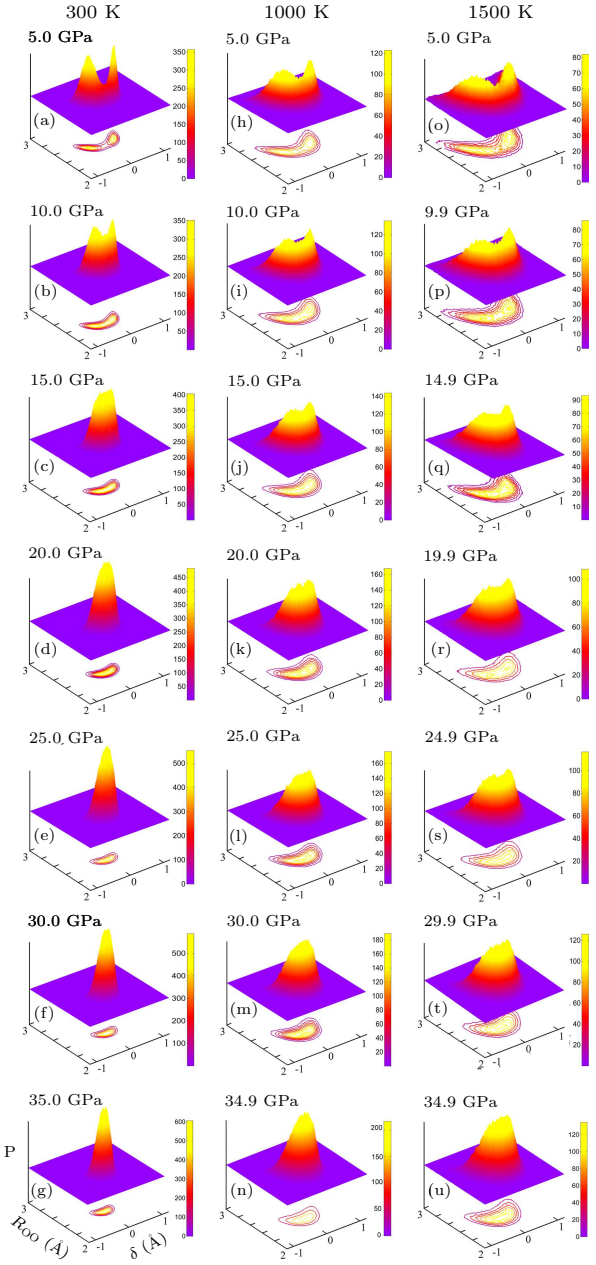


Fig. 3. The hydrogen atom probability distribution functions $P(\delta, R_{OO})$, as a function of the hydrogen atom position relative to the midpoint of the two nearest oxygen atoms (δ) and the distance between the two nearest oxygen atoms (R_{OO}) in MD simulations at 300, 1000 and 1500 K. The distribution functions are smoothed for presentation and symmetrized about $\delta = 0$ Å.

We start our discussion with the results at 300 K. At 5.0 GPa, the hydrogen-atom distribution is clearly double-peak, corresponding to an asymmetric structure (Fig. 3(a)). This asymmetric feature weakens upon increasing pressure, and the distribution finally becomes single-peak, which indicates a symmetric structure. The estimation of symmetrization pressure can be improved quantitatively by applying Landau's second-order phase-transition theory, where we plot the probability distribution function of the hydrogen atom as a function of δ using $P = A\delta^4 + B\delta^2 + C$. When the quadratic coefficient B equals zero, the system is at the second-order phase-transition point. Table S3 and Fig. S1b show that 17.0 GPa is the phase-transition pressure for δ-AlOOH at 300 K, as zero falls within the 95% confidence interval of the quadratic coefficient B. Bronstein *et al.*[24] reported that the hydrogen bond in δ-AlOOH symmetrizes at around 15–20 GPa in standard molecular dynamics, in good agreement with our results.

At 1000, 1500 and 2000 K, the hydrogen-atom distributions change upon compression in a similar manner to those at 300 K, except that the symmetrization pressure is ∼25.0 GPa at 1000 K (Figs. 3(l) and S1e), ∼29.9 GPa at 1500 K (Figs. 3(t) and S1h) and ∼34.9 GPa at 2000 K (Fig. S1k). The details of determining the distribution shape and transition pressure at 300–2000 K are demonstrated in the supplementary materials (Fig. S1, Tables S2–S6, Texts S1 and S2). It can be seen that the symmetrization pressure of δ-AlOOH depends positively on temperature according to the following relationship: $P\,(\mathrm{GPa}) = 13.9\,(\mathrm{GPa}) + 0.01\,(\mathrm{GPa/K}) \times T\,(\mathrm{K})$.

When temperature further increases, two scenarios exist. In the case that δ-AlOOH possesses asymmetric hydrogen bond at low temperature, the increase of thermal uncertainty results in larger hydrogen-atom distribution probabilities at smaller R_{OO}. The system thus becomes less asymmetric, and this effect can be seen by comparing the 5.0 GPa results at 300, 1000 and 1500 K. However, when the hydrogen bond in δ-AlOOH is already symmetric at a low temperature, the increase of thermal uncertainty results in larger hydrogen-atom distribution probabilities at larger R_{OO}. Consequently, the system becomes less symmetric under increasing temperature, and the ∼20.0 GPa results at 300, 1000 and 1500 K is an example confirming this effect. Moreover, this is the main reason for the fact that the symmetrization pressure of δ-AlOOH increases with temperature.

The calculated isothermal zero-pressure bulk moduli (K_0) of δ-AlOOH with asymmetric or symmetric hydrogen bond at different temperatures that were found by fitting the Birch–Murnaghan equation of state[31] are listed in Table 1. When K_0' is 5.0, the theoretical K_0 values at 0 K for δ-AlOOH with asymmetric hydrogen bond based on DFT calculated in the previous study[16] and in the present study are 167 GPa and 159 GPa, respectively. When K_0' is 4.3, the DFT K_0 values at 0 K for δ-AlOOH with symmetric hydrogen bond calculated in the previous study[16] and in

the present study are 205 GPa and 199 GPa, respectively. Therefore, our calculated 0 K DFT K_0 values are close to those calculated in the previous study.[16] With K_0' fixed at 4, the 300 K K_0 obtained by our simulations for δ-AlOOH with asymmetric hydrogen bond is 171 GPa, 19 GPa greater than the 300 K K_0 obtained in experiments ($K_0 = 152$ GPa);[14] the 300 K K_0 by our MD simulations for δ-AlOOH with symmetric hydrogen bond is 196 GPa, 23 GPa smaller than the experimental one obtained by Sano-Furukawa *et al.*[14] (Fig. 4). When K_0' is 3.7, K_0 at 300 K for δ-AlOOH with symmetric hydrogen bond calculated by our MD data ($K_0 = 203$ GPa) is 13 GPa greater than the data $K_0 = 190$ GPa obtained experimentally by Mashino *et al.*[32] Additionally, using the 300 K experimental pressure and volume data,[14] we have calculated K_0 to be 226 GPa with K_0' being 3.7. It can be seen that the 300 K experimental K_0 for δ-AlOOH with symmtric hydrogen bond by Sano-Furukawa *et al.*[14] and Mashino *et al.*[32] have a 36 GPa discrepancy. Despite the discrepancies for K_0 calculated by our 300 K MD data with those reported by previous experiments, our calculated 300 K K_0 for δ-AlOOH with symmetric hydrogen bond lies between the 300 K experimental K_0 values reported by Sano-Furukawa *et al.*[14] and Mashino *et al.*[32]

Table 1. Zero-pressure bulk moduli, pressure derivatives and zero-pressure volumes of δ-AlOOH.

Temperature,	δ-AlOOH with asymmetric hydrogen bond				δ-AlOOH with symmetric hydrogen bond			
Method	K_0 (GPa)	K_0'	V_0 (Å^3)	Pressure (GPa)	K_0 (GPa)	K_0'	V_0 (Å^3)	Pressure (GPa)
0 K, DFT[a]	173	4.0	57.76	5.0∼30.0	212	4.0	56.71	35.0∼55.0
0 K, DFT[a]	159	5.0	57.92	5.0∼30.0	199	4.3	56.96	35.0∼55.0
0 K, DFT[16]	167	5.0	58.61	0∼30	205	4.3	57.57	30∼60
300 K, MD[a]	171	4.0	58.09	5.0∼15.0	196	4.0	57.60	20.0∼35.0
300 K, MD[a]					203	3.7	57.48	20.0∼35.0
300 K, exp.[14]	152	4.0	56.408	0∼10	219	4.0	55.47	10∼63.5
300 K, exp.[32]					190	3.7	56.374	
300 K, exp.[14]					226	3.7	55.392	10∼63.5
1000 K, MD[a]	159	4.0	59.75	5.0∼20.0	175	4.0	59.25	25.0∼45.0
1500 K, MD[a]	149	4.0	61.06	9.9∼27.9	168	4.0	60.25	34.9∼49.9
2000 K, MD[a]					160	4.0	61.30	34.9∼55.9

[a]This work.

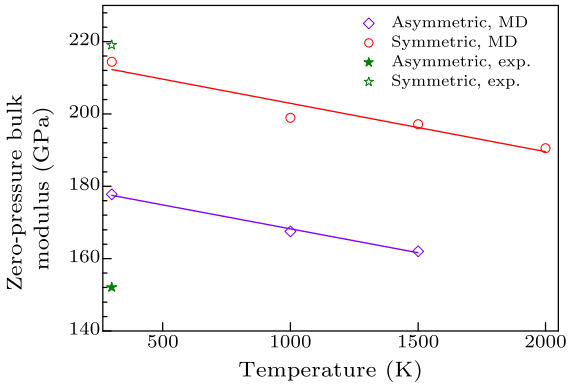


Fig. 4. The value of K_0 for δ-AlOOH with asymmetric or symmetric hydrogen bond as a function of temperature, with $K_0' = 4$. The experimental K_0 are derived with K_0' being fixed to 4.[14] For δ-AlOOH with asymmetric hydrogen bond (purple line) K_0 (GPa) = 181 (GPa) − 0.013 (GPa/K) × T (K); for δ-AlOOH with symmetric hydrogen bond (red line) K_0 (GPa) = 216 (GPa) − 0.013 (GPa/K) × T (K).

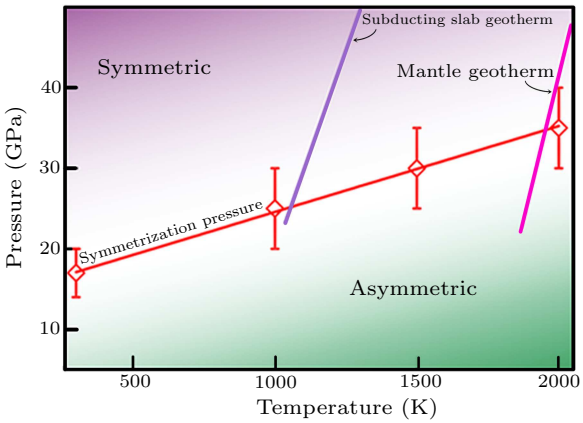


Fig. 5. Symmetrization pressure as a function of temperature (red line) along with the mantle geotherm (magenta line)[33] and subducting slab geotherm (purple line).[34] The open red diamonds represent symmetrization pressures at different temperatures. The fitted line represents the function P (GPa) = 13.9 (GPa) + 0.01 (GPa/K) × T (K). The error bars are derived from data in Tables S3–S6 and Fig. S3, from which the upper and lower limits of symmetrization pressures can be determined at different temperatures.

Symmetrization behavior induces anomalous increases in the bulk moduli. For example, due to the symmetrization of hydrogen bond, K_0 increases from 173 GPa to 212 GPa (39 GPa difference, ∼23%) at 0 K and increases from 149 GPa to 168 GPa (19 GPa difference, ∼13%) at 1500 K, fixing K_0' at 4. Additionally, K_0 decreases with temperature, described by K_0 (GPa) = 181 (GPa) − 0.013 (GPa/K) × T (K) for δ-AlOOH with asymmetric hydrogen bond and K_0 (GPa) = 216 (GPa) − 0.013 (GPa/K) × T (K) for δ-AlOOH with symmetric hydrogen bond (Fig. 4).

Phase Egg ($AlSiO_3OH$) decomposes into δ-AlOOH and stishovite at pressures above 23.0 GPa and temperatures below 1473 K.[17] At 1473 K, the symmetrization pressure of the hydrogen bond in δ-AlOOH is estimated to be 28.6 GPa, according to the relationship: P (GPa) = 13.9 (GPa) + 0.01 (GPa/K) × T (K). Additionally, nuclear quantum effects would decrease the symmetrization pressure of the hydrogen bond in δ-AlOOH about 5 GPa according to the study

by Bronstein *et al.*[24] As a result, the symmetrization pressure of hydrogen bond in δ-AlOOH is predicted to be around 23.6 GPa, close to the decomposition pressure of phase Egg. Thus we can deduce that δ-AlOOH would be generated with a hydrogen bond that is completely symmetric or close to symmetric at the top of the lower mantle. Despite the variation in the subducting slab temperature caused by many factors, such as its age and the subduction rate,[17] the dP/dT of the cold subducting slab is greater than 0.01 GPa/K,[33,35,36] ensuring that when the cold subducting slab descends, the pressure in the cold subducting slab increases more rapidly than the predicted symmetrization pressure of δ-AlOOH as temperature increases (Fig. 5). Consequently, whenever the hydrogen bond in δ-AlOOH is slightly non-symmetric, it would rapidly become completely symmetric as the cold subducting slab increases in depth. Therefore, δ-AlOOH is predicted to stabilize in symmetric structure from its birthplace or somewhere slightly deeper to the CMB along the cold subducting slabs.

In summary, we have examined the behavior of δ-AlOOH using first-principles calculations. A special focus was placed on the influence of finite-temperature statistical effects on the pressure-induced hydrogen-bond symmetrization and bulk modulus. The symmetrization pressure of hydrogen bond in δ-AlOOH is found to be ∼17.0 GPa at 300 K and increases with temperature according to the following function $P\,(\mathrm{GPa}) = 13.9\,(\mathrm{GPa}) + 0.01\,(\mathrm{GPa/K}) \times T\,(\mathrm{K})$. It can be predicted that δ-AlOOH stabilizes in the structure with symmetric hydrogen bond from its birthplace or somewhere slightly deeper to the CMB along the cold subducting slabs. The δ-AlOOH bulk modulus increases anomalously by hydrogen-bond symmetrization and decreases with temperature: for δ-AlOOH with asymmetric hydrogen bond $K_0\,(\mathrm{GPa}) = 181.0\,(\mathrm{GPa}) - 0.013\,(\mathrm{GPa/K}) \times T\,(\mathrm{K})$, for δ-AlOOH with symmetric hydrogen bond $K_0\,(\mathrm{GPa}) = 216.0\,(\mathrm{GPa}) - 0.013\,(\mathrm{GPa/K}) \times T\,(\mathrm{K})$, with K_0' fixed at 4.

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Supplementary material for

Hydrogen-bond symmetrization of δ-AlOOH*

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Text S1. Quartic or quadratic functions to fit the hydrogen atoms distribution curves, and the analyses how to determine the curve shapes through the quartic and quadratic coefficients

The two-dimensional distribution curves and the quartic or quadratic distributions fitting the real distributions are described in Figure S1, from which the symmetrization pressure can be estimated visually. To determine the symmetrization pressure and hydrogen-bond state from a more rigorous perspective, the curve shapes of the following function (1) under different conditions[1] are analyzed.

$$P = A\,\delta^4 + B\,\delta^2 + C \qquad (1)$$

The first-order derivative of function (1) is as follows:

$$P' = 4A\,\delta^3 + 2B\,\delta\,, \qquad (2)$$

where P is the distribution probability of the hydrogen atoms, A is the quartic coefficient, B is the quadratic coefficient, C represents a constant.

It is obvious that the quartic coefficient A cannot be positive, as all the curves in Figure S1 open downward. For the case of $A < 0$, there are three scenarios for B. When $B > 0$, function (1) has three extreme points (one local minimum at $\delta = 0$ and two local maxima) judged from function (2), indicative of a double-peak curve; when $B < 0$, function (1) has only one extreme point (one maximum at $\delta = 0$), showing an obvious single-peak curve; finally, $B = 0$ represents the transition state from a double-peak to single-peak distribution[1]. $A = 0$ represents a single-peak quadratic curve, accompanied by $B < 0$ for curves that open downward. As a result, we can estimate the transition pressure from the curve shapes determined by A and B values in function (1). The possible A and B values and the corresponding curve shapes and δ-AlOOH structures are tabulated in Table S2, and the 95% confidence intervals for the A and B coefficients of the fitted curves around the symmetrization pressures are tabulated in Tables S3-S6.

Text S2. How to judge the distribution curve based on the estimated 95% confidence intervals of quartic coefficient A and quadratic coefficient B

At 300 K and 15.0 GPa (Table S3), the 95% confidence intervals suggest that $A < 0$ and $B > 0$, indicating that the distribution curve at 300 K and 15.0 GPa is double-peak. These results agree well with the curve shape in Figure S1 (a), which is obviously double-peak. At 300 K and 17.0 GPa, $A < 0$ and $B = 0$, suggesting the coexistence of asymmetric and symmetric phases (Figure S1 (b)). At 300 K and 20.0 GPa, the distribution curve is determined to be single-peak, characterized by $A = 0$ and $B < 0$ (Figure S1 (c)). A or B is regarded as zero as long as zero is included in its 95% confidence interval. As a result, the transition pressure at 300 K is 17.0 GPa. For 1000 K, it can be inferred from Table S4 that $A < 0$ and $B > 0$ at 20.0 GPa, $A < 0$ and $B = 0$ at 25.0 GPa, and $A < 0$ and $B < 0$ at 30.0 GPa. Combined with Table S2, the curve shape can be determined to be double-peak at 20.0 GPa and single-peak at 30.0 GPa, consistent with Figures S1 (d) and (f); the symmetrization pressure is determined to be approximately 25.0 GPa, at which pressure the

hydrogen-atom distribution is slightly broad (Figure S1 (e)). For 1500 and 2000 K (Tables S5 and S6), the symmetrization pressure is approximately 29.9 GPa and 34.9 GPa, respectively, determined by similar a method to that used for 300 and 1000 K.

Table S1 The lattice constants from different experiments and calculations.

	Experiments			Calculations with First-principles				
Methods/ Functions	Powder XRD[2]	Neutron diffraction[3]	Single-crystal XRD[4]	GGA[5]	LDA[6]	GGA-PBE[7]	GGA-PBE[8]	GGA-PBE[a]
a (Å)	4.713	4.715	4.713	4.723	4.657	4.788	4.788	4.763
b (Å)	4.224	4.288	4.222	4.214	4.141	4.275	4.275	4.254
c (Å)	2.833	2.836	2.832	2.861	2.829	2.877	2.877	2.861

[a] This work.

Table S2 The possible A and B values and the corresponding curve shapes and δ-AlOOH phases.

A	B	Shape of the curve	Phase
	> 0	Double-peak	Asymmetric phase
< 0	= 0	Intermediate shape between double-peak and single-peak	Coexistence of asymmetric and symmetric phases
	< 0	Single-peak	Symmetric phase
= 0	< 0	Single-peak	Symmetric phase

Table S3 The 95% confidence intervals of quartic coefficient A and quadratic coefficient B around symmetriztion pressure at 300 K.

	15.0 GPa	17.0 GPa	20.0 GPa
A	–498365.40 ~ –337654.60	–167095.20 ~ –146548.00	–99552.49 ~ 64432.64
B	12154.88 ~ 18177.76	–369.2683 ~ 1815.873	–19309.63 ~ –13164.04

Table S4 The 95% confidence intervals of quartic coefficient A and quadratic coefficient B around symmetriztion pressure at 1000 K.

	20.0 GPa	25.0 GPa	30.0 GPa
A	–78262.55 ~ –48123.35	–66826.53 ~ –48227.08	–23615.99 ~ 185.38
B	3175.08 ~ 5679.42	–390.15 ~ 1155.32	–6730.14 ~ –4752.42

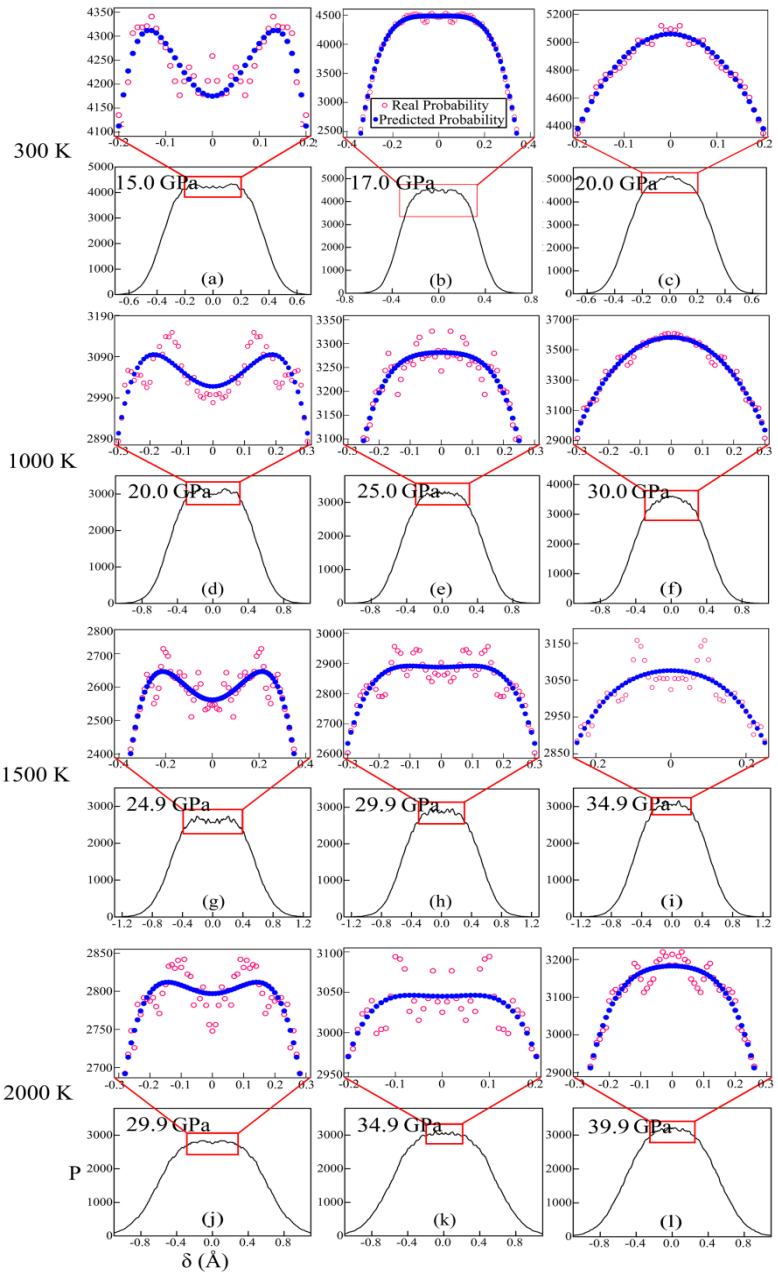
Table S5 The 95% confidence intervals of quartic coefficient A and quadratic coefficient B around symmetriztion pressure at 1500 K.

P	24.9 GPa	29.9 GPa	34.9 GPa
A	–48435.37 ~ –34258.35	–55194.72 ~ –24607.38	–49264.07 ~ 14960.41
B	2954.05 ~ 4550.50	–473.42 ~ 2068.15	–3929.165 ~ –201.0402

Table S6 The 95% confidence intervals of quartic coefficient A and quadratic coefficient B around symmetriztion pressure at 2000 K.

P	29.9 GPa	34.9 GPa	39.9 GPa
A	–47061.85 ~ –24395.16	–121462.6 ~ –22.54422	–57287.42 ~ –19318.43
B	637.8027 ~ 2282.001	–1718.292 ~ 2832.86	–2600.105 ~ –219.4737

Fig. S1 The hydrogen atom probability distribution functions, P (δ), as a function of δ in MD simulations around symmetrization pressures, at 300, 1000, 1500 and 2000 K. The distribution functions are smoothed for presentation and symmetrized about δ = 0 Å. In the magnified part, the real hydrogen atom distributions are plotted in red open circles, and the quartic or quadratic distributions used to fit the real distributions are in blue solid circles. The fitted δ ranges limited by red rectangles center at δ = 0 Å and extend toward two sides till the real distribution curves became almost linear, containing enough data to determine the curves shapes.



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