

Supporting Information for “Hydrogen diffusion in the lower mantle revealed by machine learning potentials”

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Text S1 hydrogen diffusion in Al-bearing bridgmanite

Muir and Brodholt (2018) reported that most water in bridgmanite may be incorporated via $\text{Al}^{3+}\text{-H}^+$ pairs throughout the lower mantle. Therefore, we investigate the hydrogen diffusion in Al-bearing bridgmanite considering $(\text{Al} + \text{H})_{\text{Si}}$ defects using the on-the-fly machine learning force field (MLFF) trained from *ab initio* data.

We consider three supercells containing 80 ($2 \times 2 \times 1$ for *Pbnm* bridgmanite), 360 ($3 \times 3 \times 2$ for *Pbnm* bridgmanite), and 2880 ($6 \times 6 \times 4$ for *Pbnm* bridgmanite) atoms. The water content of the system is controlled by substituting different numbers of Si atoms with Al atoms and hydrogen atoms, generating $(\text{Al} + \text{H})_{\text{Si}}$ defects that are evenly distributed in the supercell. All *ab initio* calculations and MLFF generations are performed using VASP (Kresse and Furthmuller, 1996). For *ab initio* calculations, we adopt the PBEsol approximation (Perdew et al., 2008) with the projector augmented wave (PAW) method (Kresse and Joubert, 1999). The core radii of O ($2s^2 2p^4$), Si ($3s^2 3p^2$), Mg ($2p^6 3s^2$), Al ($3s^2 3p^1$), and H ($1s^1$) are 0.820 Å, 1.312 Å, 1.058 Å, 1.402 Å, and 0.370 Å, respectively. We employ a 500-eV energy cutoff and sample the Brillouin zone at the Γ point. All molecular dynamics (MD) simulations are performed in the NVT ensemble at 2000 K controlled by the Nosé-Hoover thermostat (Hoover, 1985) with a time step of 0.5 fs. During MD simulations, MLFFs are trained using total energies, forces, and stress tensors from automatically selected DFT structures. Similar to the DeePMD method in the main text, the potential energy of the system is decomposed as the sum of local energies derived from the local environments of atoms. A Bayesian error estimate is applied to decide between DFT or MLFF forces for the MD simulation. If the predicted errors exceed the threshold, a new reference structure will be chosen and recalculated, based on which the coefficients of the MLFF will be adjusted. A detailed description of the MLFF approach can be found in Jinnouchi et al. (2019a) and Jinnouchi et al. (2019b).

We initiate our on-the-fly training with a small system ($\text{Mg}_{16}\text{Si}_{14}\text{Al}_2\text{O}_{48}\text{H}_2$) and extend the training set by continuing the on-the-fly training using larger systems ($3 \times 3 \times 2$ for *Pbnm* bridgmanite) with various water contents (0.12–1.68 wt%) at different pressures (24, 25, and 26 GPa). The Al content in the DFT training set ranges from 0.37–5.04 wt% and is proportional to the water content. The final training set

consists of 1800 DFT configurations and the corresponding MLFF is refitted for prediction-only MD runs. We compare the energies, atomic forces, and stresses from the MLFF to those from DFT calculations for 200 configurations that are not included in the training set, and the root-mean-square errors of the energies, atomic forces, and stresses are $0.55 \text{ meV atom}^{-1}$, $0.09 \text{ eV \AA}^{-1}$, and 0.09 GPa , respectively. Since the training set only contains one mineral phase with one hydrogen substitution mechanism, and the MLFF is limited to $\sim 2000 \text{ K}$ and $24\text{--}26 \text{ GPa}$, this error is much smaller than our MLP introduced in the main text.

Prediction-only MD simulations are performed with the MLFF at 2000 K and 25 GPa for different supercells of bridgmanite with different water contents ($\text{Mg}_{16}\text{Si}_{14}\text{Al}_2\text{O}_{48}\text{H}_2$, $C_{\text{water}} = 1.12 \text{ wt\%}$; $\text{Mg}_{72}\text{Si}_{70}\text{Al}_2\text{O}_{216}\text{H}_2$, $C_{\text{water}} = 0.25 \text{ wt\%}$; $\text{Mg}_{576}\text{Si}_{568}\text{Al}_8\text{O}_{1728}\text{H}_8$, $C_{\text{water}} = 0.12 \text{ wt\%}$). For comparison, the same supercells of bridgmanite with $(\text{Mg} + 2\text{H})_{\text{Si}}$ defects are simulated using the MLP ($\text{Mg}_{17}\text{Si}_{15}\text{O}_{48}\text{H}_2$, $C_{\text{water}} = 1.12 \text{ wt\%}$; $\text{Mg}_{73}\text{Si}_{71}\text{O}_{216}\text{H}_2$, $C_{\text{water}} = 0.25 \text{ wt\%}$; $\text{Mg}_{580}\text{Si}_{572}\text{O}_{1728}\text{H}_8$, $C_{\text{water}} = 0.12 \text{ wt\%}$). The simulation time is $100\text{--}200 \text{ ps}$ for each run and 10 independent runs with different initial velocity distributions are performed for each system to evaluate the uncertainties. Two 100-ps trajectories of hydrogen in the largest systems with the $(\text{Al} + \text{H})_{\text{Si}}$ defect and the $(\text{Mg} + 2\text{H})_{\text{Si}}$ defect are shown in Fig. S7a and Fig. S7b, respectively. The hydrogen diffusion coefficients in all those systems are derived from the mean square displacements and plotted in Fig. S8. For $\text{Mg}_{17}\text{Si}_{15}\text{O}_{48}\text{H}_2$ with the $(\text{Mg} + 2\text{H})_{\text{Si}}$ defect, we used both the MLP and MLFF methods to perform simulations under completely identical conditions, and obtained very close diffusion coefficients (with only a 3.4% difference, Fig. S8a), verifying the consistency of the results from these two methods. Consistent with the MD trajectory of hydrogen associated with $(\text{Al} + \text{H})_{\text{Si}}$ reported by Muir and Brodholt (2018), hydrogen atoms are not strongly bound to a specific oxygen atom in a fixed lattice site, but are able to diffuse far from the Al^{3+} ion. In addition, at 2000 K and 25 GPa , the hydrogen diffusion coefficients for $(\text{Al} + \text{H})_{\text{Si}}$ and $(\text{Mg} + 2\text{H})_{\text{Si}}$ both fall within the order of magnitude of $10^8 \text{ m}^2 \text{ s}^{-1}$, exceeding $(2\text{H})_{\text{Mg}}$ and $(4\text{H})_{\text{Si}}$ by at least an order of magnitude (see Fig. 5). We conclude that $(\text{Al} + \text{H})_{\text{Si}}$ and $(\text{Mg} + 2\text{H})_{\text{Si}}$ exhibit remarkably similar hydrogen diffusion patterns with closely matching hydrogen diffusion coefficients at the uppermost lower mantle conditions, considering all three water and aluminum contents. Owing to this intrinsic similarity between $(\text{Al} + \text{H})_{\text{Si}}$ and $(\text{Mg} + 2\text{H})_{\text{Si}}$, we propose that the hydrogen diffusion in these two defects can be treated analogously, and our discussions about $(\text{Mg} + 2\text{H})_{\text{Si}}$ might well

apply to (Al + H)_{Si} too.

Text S2 Defect distribution in the supercell

To accurately quantify the distribution of defects in the supercell, we used the average inter-defect distance of nearest neighbors (ξ) as a collective variable defined as

$$\xi = \sum_{i=1}^N \frac{d_i^{\min}}{N} \quad (\text{S1})$$

where N is the total number of defects in the system, and $d^{\min}$ is the distance between a defect and its nearest neighboring defect. Taking (2H)_{Mg} as an example, given positions of Mg atoms that will be substituted by hydrogen atoms, i.e., the positions of defects in the initial configuration for MD simulations, we compute the distance between all defects and their respective nearest neighboring defects, i.e., $d^{\min}$, which are then averaged to derive ξ . This parameter can quantify how far away the different water-containing defects are. Specifically, small ξ means that defects tend to gather into clusters, and large ξ means that the defects are dispersed with the largest ξ corresponding to the uniform distribution of defects.

In order to determine the stability of different defect distributions and find the most energy-favored one, we conduct a simple Monte Carlo simulation. We generate 100 different hydrous bridgmanite (Mg₆₀Si₆₄O₁₉₂H₈) configurations with (2H)_{Mg} defects, among which 98 configurations are randomly generated using AtomsK (Hirel, 2015), that is, 4 of the 64 Mg atoms are randomly selected to be substituted by hydrogen atoms. The rest two configurations include one with the largest ξ where defects are evenly distributed in the supercell, and the other with the smallest ξ where 4 nearest Mg atoms within a unit cell were replaced with H atoms. We calculated the enthalpy of each configuration using both MLP and DFT methods, as shown in Fig. S9. For the MLP results, although the different defect distributions lead to some variation in the enthalpy of the system, the standard deviation is only 6.06 meV atom⁻¹ enthalpies are almost identical considering the uncertainty of our MLP, which is smaller than the RMSE of our MLP (RMSE = 6.39 meV atom⁻¹). This is more pronounced in the DFT results, where the standard deviation of the enthalpy is as low as 0.46 meV atom⁻¹, which is far lower than the theoretical uncertainty of calculating enthalpy using the DFT method (tens of meV atom⁻¹, Wang et al., 2021). Therefore, we argue that the enthalpy variation in Fig. S9

is negligible and all random configurations with different defect distributions may have almost the same enthalpy. Therefore, it may be true that the probability of various defect distributions occurring in nature is approximately equal, and it is difficult to find a specific defect configuration that is preferred in terms of energy. Thus, we can directly use any type of defect distribution configuration for diffusion simulation, instead of searching for the most stable one.

We investigate the impact of defect distribution on hydrogen diffusion by simulating and calculating the hydrogen diffusion coefficients using multiple different configurations with randomly distributed defects. We then compared the results with those for which defects are uniformly distributed, in order to quantify how the defect distribution ultimately affects the hydrogen diffusion coefficient. We choose two representative bridgmanite systems at 25 GPa and 2000 K: $\text{Mg}_{16368}\text{Si}_{16384}\text{O}_{49152}\text{H}_{32}$ (0.0175 wt% water, Fig. S10a) and $\text{Mg}_{8128}\text{Si}_{8192}\text{O}_{24576}\text{H}_{128}$ (0.140 wt% water, Fig. S10b). The blue square represents the average value of hydrogen diffusion coefficients calculated from 10 independent simulations with different initial velocity distributions, considering the same supercell containing uniformly distributed defects. The orange square represents the average result obtained from 10 different supercells with randomly distributed defects. The results suggest that while using a random defect distribution may slightly increase the uncertainty of the calculated diffusivity, the impact on the mean is negligible compared to the calculation error, validating the result obtained from the uniform defect distribution in the manuscript.

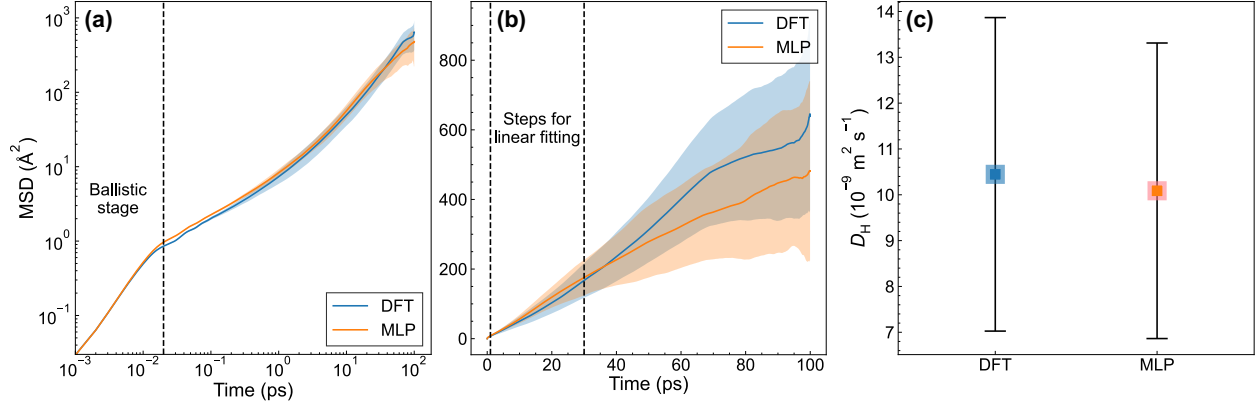


Figure S1: Comparisons of mean square displacements (MSD) and hydrogen diffusion coefficients (D_H) derived with the density functional theory (DFT) and the machine learning potential (MLP) for hydrous bridgmanite ($\text{Mg}_{15}\text{Si}_{16}\text{O}_{48}\text{H}_2$) at 3000 K and 25 GPa. The shading and the error bar represent the standard deviation of 10 independent simulations. (a) MSD as a function of the simulation time using double logarithmic axes; (b) MSD as a function of the simulation time using linear axes; (c) D_H calculated using DFT and MLP.

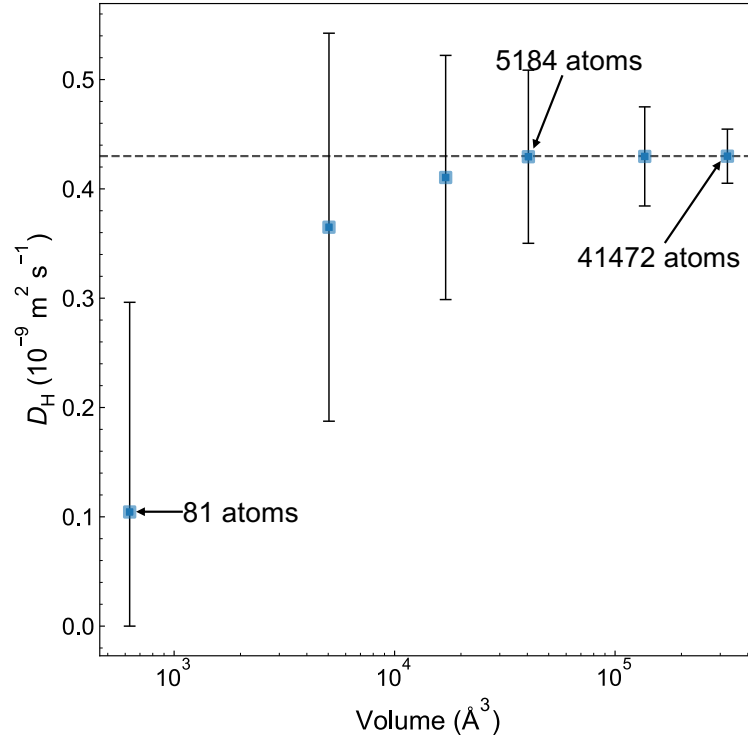


Figure S2: Hydrogen diffusion coefficients vs. supercell volumes of hydrous bridgmanite ($\text{Mg}_{0.9375}\text{SiO}_3\text{H}_{0.125}$) at 2000 K and 25 GPa. The total number of atoms is indicated. The error bar represents the 2SD of 10 independent simulations. Hydrogen diffusivities increase and converge to a constant (the dashed line) with system size.

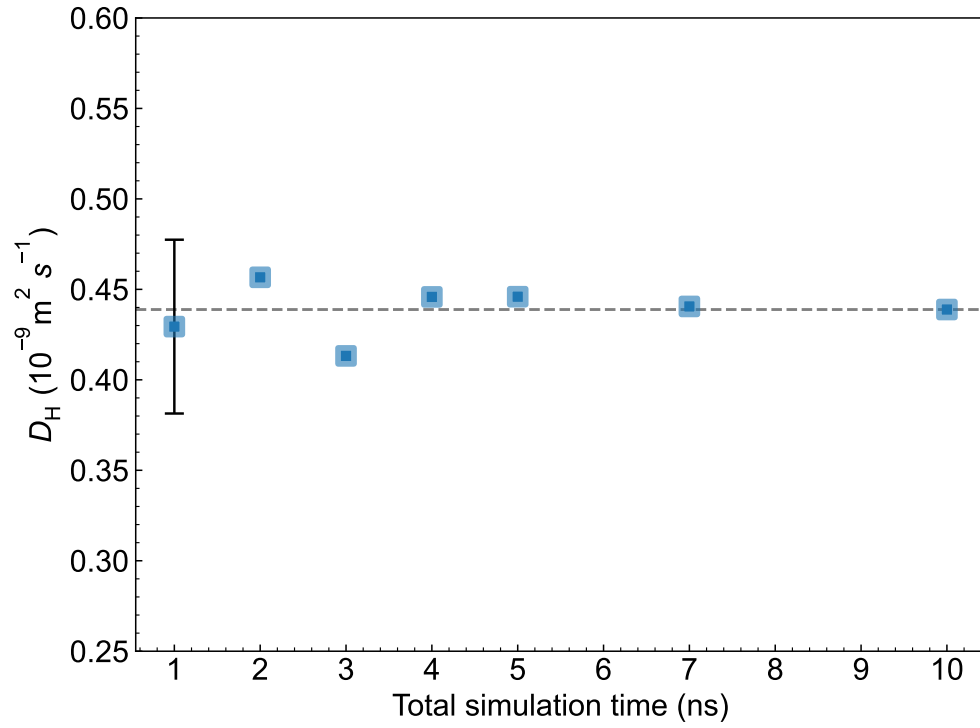


Figure S3: Hydrogen diffusion coefficients as a function of total simulation time of hydrous bridgmanite ($\text{Mg}_{960}\text{Si}_{1024}\text{O}_{3072}\text{H}_{128}$) at 2000 K and 25 GPa. The error bar represents the 2SD of 10 independent simulations with a simulation time of 1 ns.

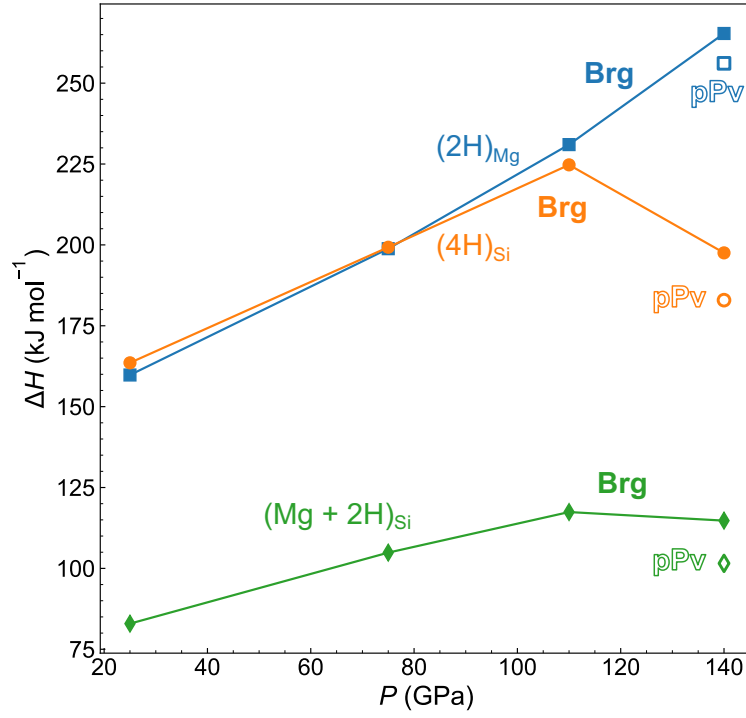


Figure S4: The activation enthalpy of hydrogen diffusion as a function of pressure for different hydrogen incorporation mechanisms. Filled and empty symbols represent bridgmanite and post-perovskite, respectively. $(2\text{H})_{\text{Mg}}$ ($\text{Mg}_{7680}\text{Si}_{8192}\text{O}_{24576}\text{H}_{1024}$), $(4\text{H})_{\text{Si}}$ ($\text{Mg}_{8192}\text{Si}_{7936}\text{O}_{24576}\text{H}_{1024}$), and $(\text{Mg} + 2\text{H})_{\text{Si}}$ ($\text{Mg}_{8704}\text{Si}_{7680}\text{O}_{24576}\text{H}_{1024}$) defects are shown in blue, orange, and green, respectively.

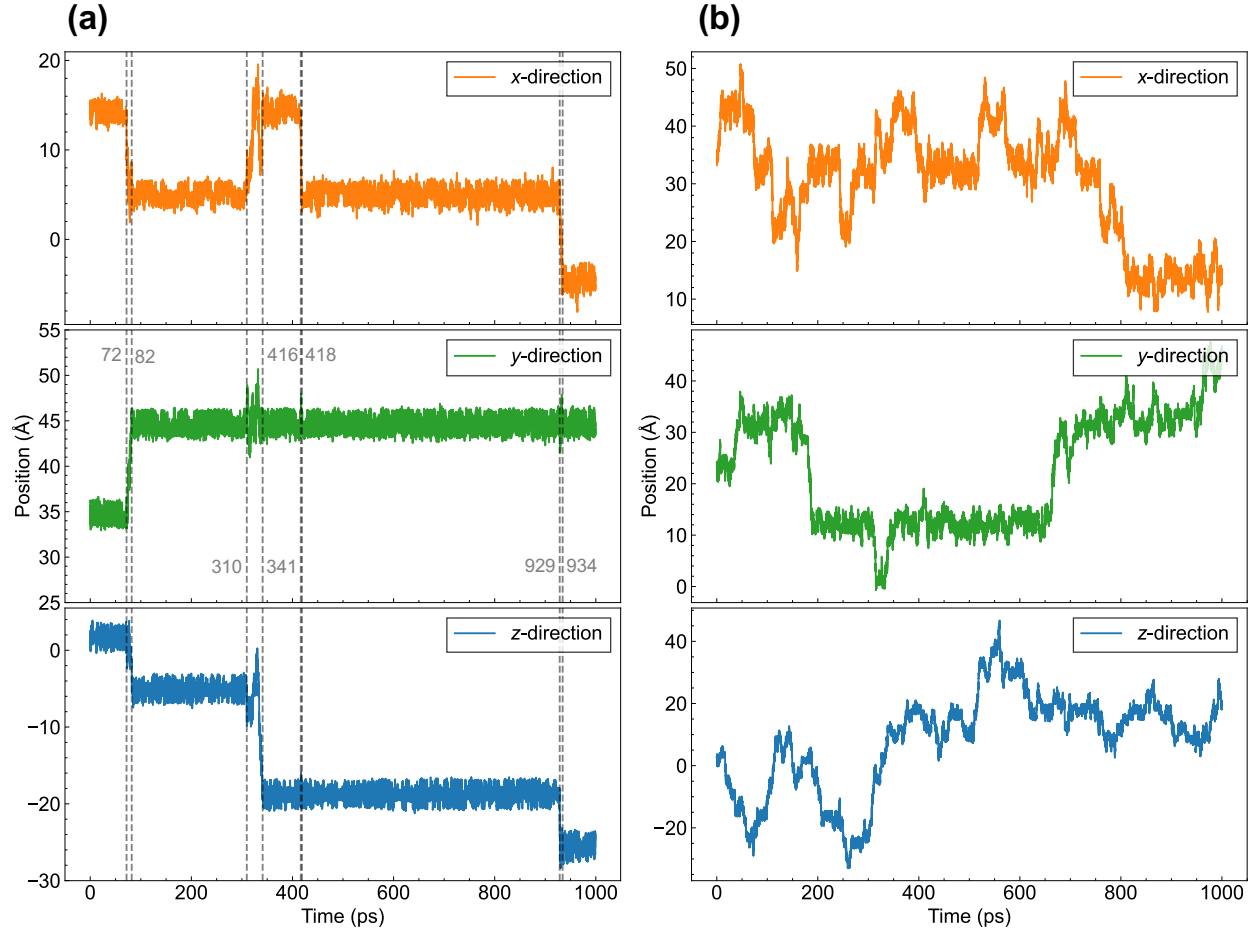


Figure S5: The atomic positions along the three crystallographic axes as a function of time in hydrous bridgmanite for (a) the $(2\text{H})_{\text{Mg}}$ defect ($\text{Mg}_{960}\text{Si}_{1024}\text{O}_{3072}\text{H}_{128}$) and (b) the $(\text{Mg} + 2\text{H})_{\text{Si}}$ defect ($\text{Mg}_{1088}\text{Si}_{960}\text{O}_{3072}\text{H}_{128}$) at 2000 K and 25 GPa. The trajectories of these atoms are shown in Fig. 3.

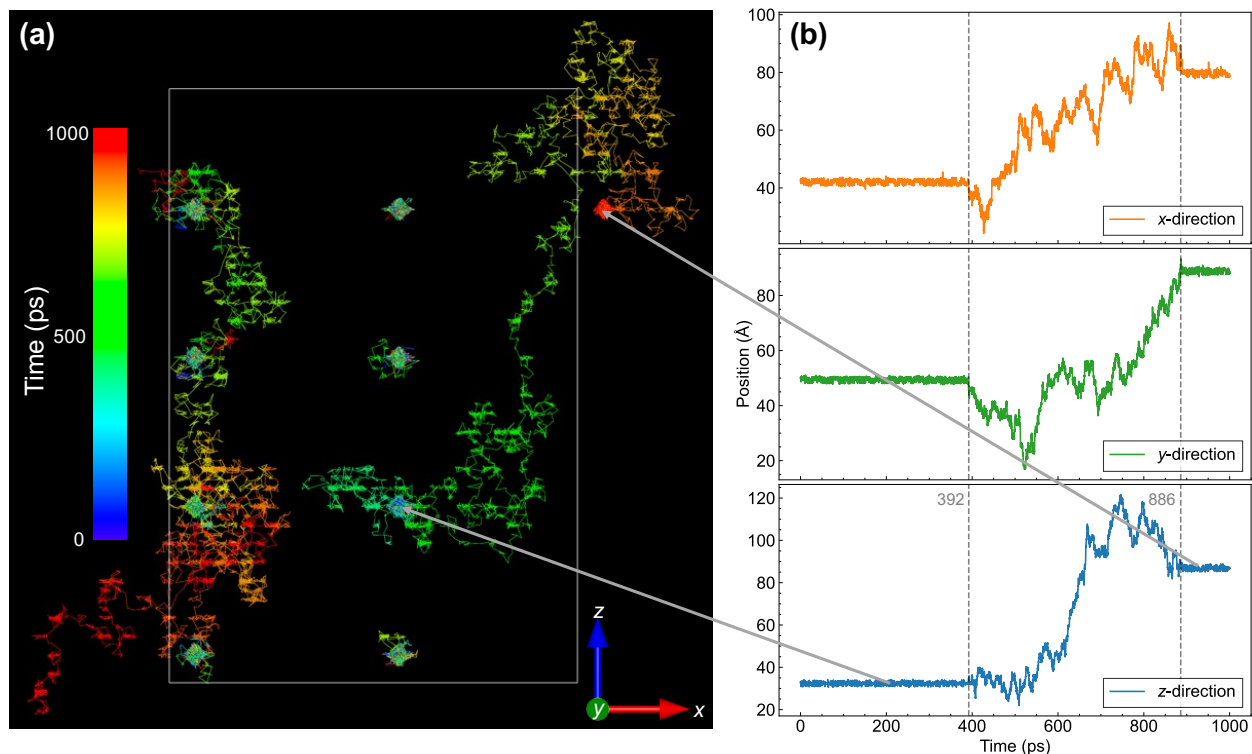


Figure S6: (a) Color mapping of the trajectory of 32 hydrogen atoms over time in hydrous bridgmanite for the $(2\text{H})_{\text{Mg}}$ defect ($\text{Mg}_{16368}\text{Si}_{16384}\text{O}_{49152}\text{H}_{32}$, $C_{\text{water}} = 0.0175 \text{ wt\%}$) at 2000 K and 25 GPa. As the simulation time increases from 0 ps to 1000 ps, the color of the trajectory changes along the visible spectrum. All atoms are omitted for clarity. (b) The atomic position along the three crystallographic axes as a function of time of one hydrogen atom (pointed by gray arrows).

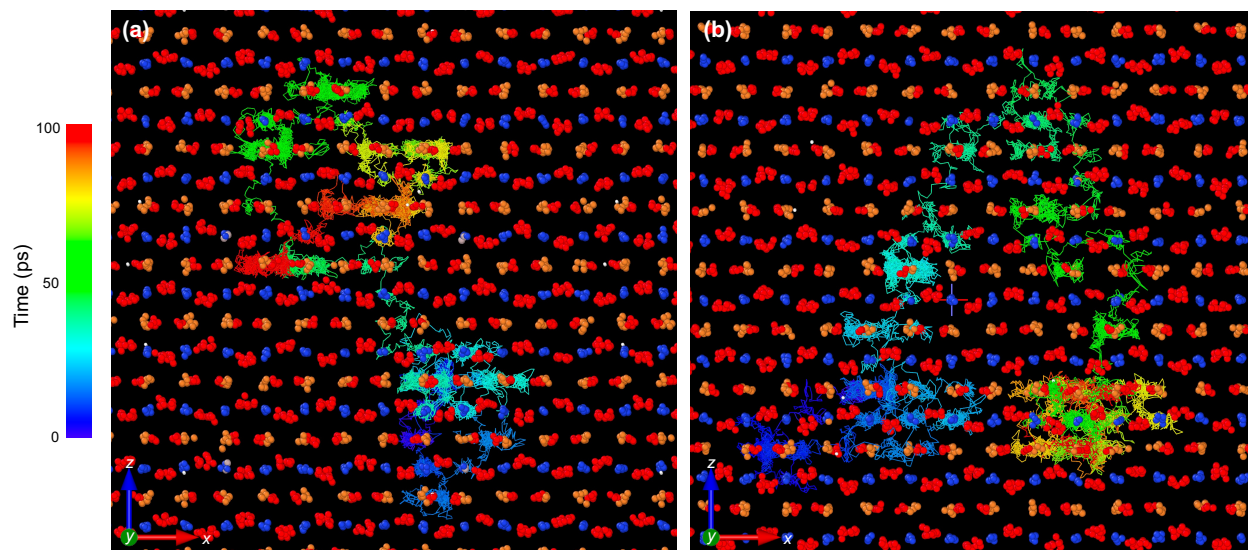


Figure S7: Color mapping of the trajectories of two hydrogen atoms over time in hydrous bridgmanite for (a) the $(\text{Al} + \text{H})_{\text{Si}}$ defect ($\text{Mg}_{576}\text{Si}_{568}\text{Al}_8\text{O}_{1728}\text{H}_8$, $C_{\text{water}} = 0.12 \text{ wt\%}$) and (b) the $(\text{Mg} + 2\text{H})_{\text{Si}}$ defect ($\text{Mg}_{580}\text{Si}_{572}\text{O}_{1728}\text{H}_8$, $C_{\text{water}} = 0.12 \text{ wt\%}$) at 2000 K and 25 GPa. As the simulation time increases from 0 ps to 100 ps, the color of the trajectory changes along the visible spectrum. Orange, blue, red, and white spheres represent magnesium, silicon, oxygen, and hydrogen, respectively.

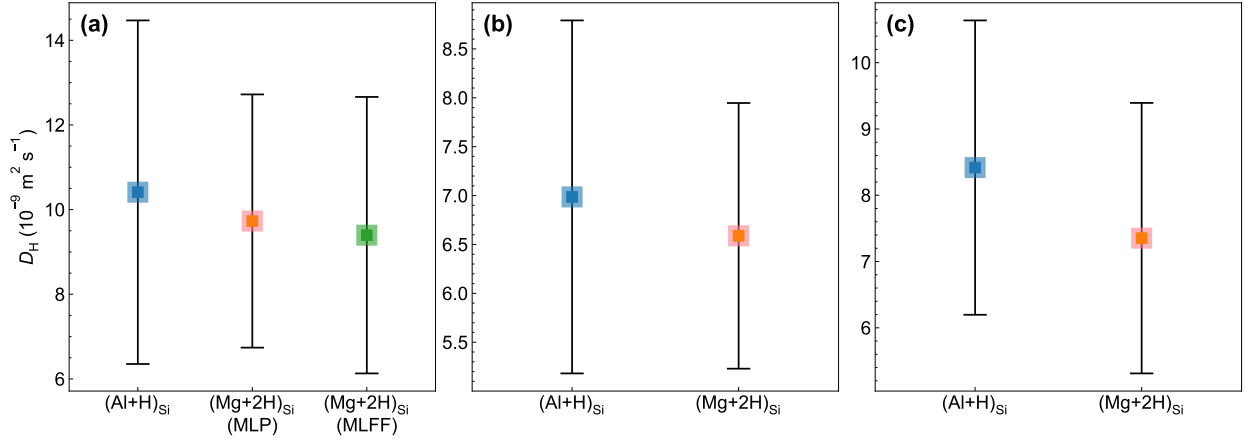


Figure S8: Comparisons of hydrogen diffusion coefficients of hydrous bridgmanite with (Al + H)_{Si} and (Mg + 2H)_{Si} defects at 2000 K and 25 GPa. (a) (Al + H)_{Si}: $\text{Mg}_{16}\text{Si}_{14}\text{Al}_2\text{O}_{48}\text{H}_2$, $C_{\text{water}} = 1.12 \text{ wt\%}$; (Mg + 2H)_{Si}: $\text{Mg}_{17}\text{Si}_{15}\text{O}_{48}\text{H}_2$, $C_{\text{water}} = 1.12 \text{ wt\%}$. (b) (Al + H)_{Si}: $\text{Mg}_{72}\text{Si}_{70}\text{Al}_2\text{O}_{216}\text{H}_2$, $C_{\text{water}} = 0.25 \text{ wt\%}$; (Mg + 2H)_{Si}: $\text{Mg}_{73}\text{Si}_{71}\text{O}_{216}\text{H}_2$, $C_{\text{water}} = 0.25 \text{ wt\%}$. (c) (Al + H)_{Si}: $\text{Mg}_{576}\text{Si}_{568}\text{Al}_8\text{O}_{1728}\text{H}_8$, $C_{\text{water}} = 0.12 \text{ wt\%}$; (Mg + 2H)_{Si}: $\text{Mg}_{580}\text{Si}_{572}\text{O}_{1728}\text{H}_8$, $C_{\text{water}} = 0.12 \text{ wt\%}$. The simulation time is 200 ps for (a) and (b), and 100 ps for (c).

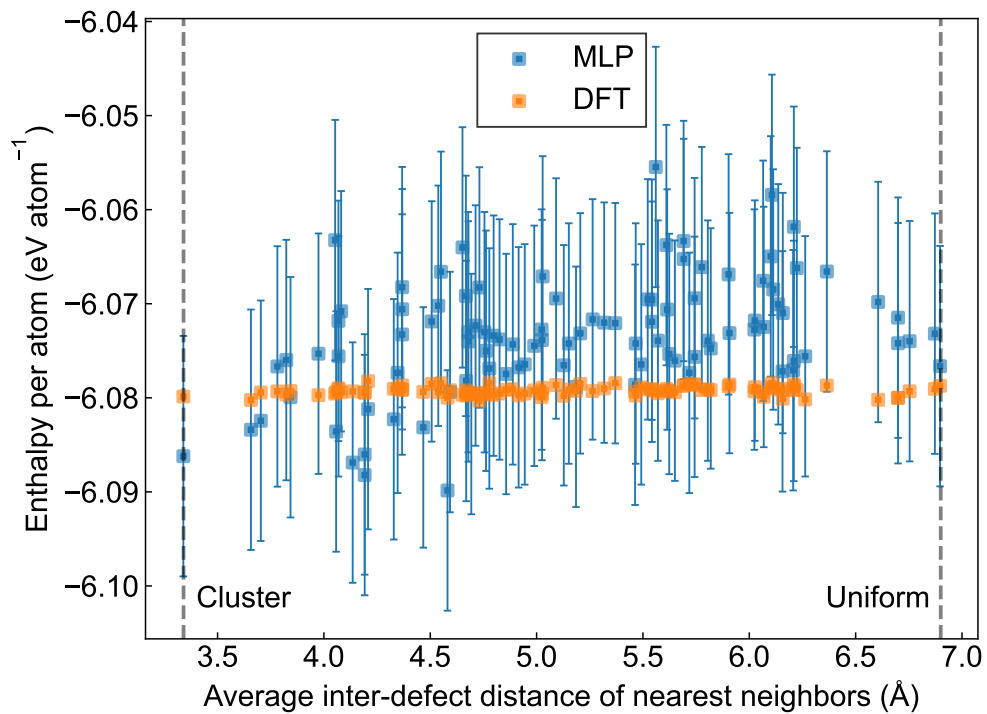


Figure S9: The static enthalpy of 100 different defect distributions of hydrous bridgmanite ($\text{Mg}_{60}\text{Si}_{64}\text{O}_{192}\text{H}_8$) calculated using DFT and MLP at 25 GPa. The error bars represent the 2RMSE of our MLP.

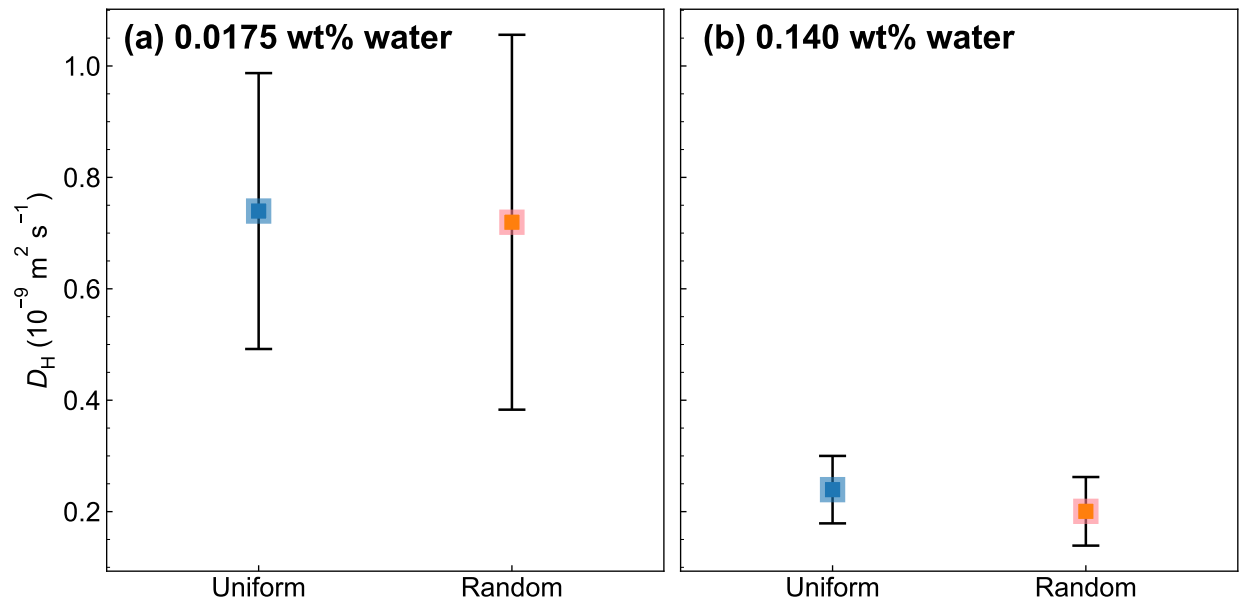


Figure S10: Comparisons of hydrogen diffusion coefficients of hydrous bridgmanite (a, $\text{Mg}_{16368}\text{Si}_{16384}\text{O}_{49152}\text{H}_{32}$; b, $\text{Mg}_{8128}\text{Si}_{8192}\text{O}_{24576}\text{H}_{128}$) calculated using uniform and random defect distributions at 2000 K and 25 GPa.

Table S1: Hydrogen diffusion coefficient of bridgmanite (Brg) and post-perovskite (pPv) at different pressures (25, 75, and 140 GPa) and temperatures (2000, 3000, and 4000 K). Pre-exponential factor (D_0) and activation enthalpy (ΔH) are shown for each pressure.

Table S2: Hydrogen diffusion coefficient and proton conductivity of bridgmanite (Brg) and post-perovskite (pPv) along an adiabatic geotherm Katsura et al. (2010).

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