

# Geophysical Research Letters®



## RESEARCH LETTER

10.1029/2026GL123823

### Key Points:

- Evolution of H-bond symmetrization in (Al, H)-SiO<sub>2</sub> was measured up to 62 GPa and 800 K by synchrotron IR and Raman spectroscopy, and XRD
- (Al, H)-SiO<sub>2</sub> undergoes H-bond symmetrization at ~30 GPa and 300 K, while elevated temperature to 800 K lowers the onset pressure to ~12 GPa
- H-bond symmetrization in (Al, H)-SiO<sub>2</sub> enables deep-water transport to the lower mantle, linking surface water to core-mantle boundary

### Supporting Information:

Supporting Information may be found in the online version of this article.

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### Citation:

Zhao, C., Mao, Z., Yu, Y., Sun, N., Fu, Y., Zhang, J., et al. (2026). Hydrogen-bond symmetrization in hydrous aluminous silica enhances deep-mantle water cycle. *Geophysical Research Letters*, 53, e2026GL123823. <https://doi.org/10.1029/2026GL123823>

Received 1 MAY 2026

Accepted 14 SEP 2026

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## Hydrogen-Bond Symmetrization in Hydrous Aluminous Silica Enhances Deep-Mantle Water Cycle

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**Abstract** (Al, H)-bearing CaCl<sub>2</sub>-type SiO<sub>2</sub> serves as a key water carrier in Earth's deep-water cycle.

Evolution of hydrogen-bond symmetrization in this phase was measured up to 62 GPa and 800 K by synchrotron infrared and Raman spectroscopy, and X-ray diffraction. It undergoes symmetrization at ~30 GPa and 300 K, while elevated temperature to 800 K lowers the onset pressure to ~12 GPa. This implies that the symmetrized phase will form directly near the base of the transition zone in (Al, H)-rich subducted slabs, and deeper in (Al, H)-poor slabs via transformation from stishovite. More importantly, this symmetrization state stiffens the crystal lattice and immobilizes hydrogen within the structure, enhancing water retention and preventing hydrogen loss during subduction to the lower mantle. Our findings suggest that this phase acts as an important deep-water reservoir capable of transporting water to the lower mantle, thereby linking the deep-water cycle from Earth's surface to core-mantle boundary.

**Plain Language Summary** The deep-water cycle fundamentally influences Earth's interior dynamics, including melting, mantle rheology, and element recycling. Although hydrous minerals transport water into the upper mantle and transition zone, most break down at the top-lower mantle. How water is stored and redistributed beyond the 660 km discontinuity remains uncertain, limiting our understanding of Earth's long-term material cycling. Recent findings suggest that (Al, H)-bearing CaCl<sub>2</sub>-type SiO<sub>2</sub> can retain weight percent of water near the core-mantle boundary conditions, demonstrating exceptional water storage capacity. These insights challenge previous assumptions about the slab dehydration limit, positioning (Al, H)-bearing CaCl<sub>2</sub>-type SiO<sub>2</sub> as a key phase in revising our understanding of water cycling in the deep-mantle. However, little is known about the physical properties of this phase at relevant lower mantle pressures and temperatures. In this study, synchrotron infrared and Raman spectroscopy, and X-ray diffraction demonstrate that under deep-mantle conditions, hydrogen-bond symmetrization in (Al, H)-bearing CaCl<sub>2</sub>-type SiO<sub>2</sub> leads to pronounced structural stiffening. Our findings reveal that hydrogen-bond symmetrization in (Al, H)-bearing CaCl<sub>2</sub>-type SiO<sub>2</sub> serves as an important deep-water reservoir with the unique capacity to transport water to the deep lower mantle, thereby linking the deep-water cycle from Earth's surface to core-mantle boundary.

## 1. Introduction

Earth's water cycle extends far beyond its surface, with subducting slabs acting as critical pathways for transporting water into the mantle (Bang et al., 2024; Cai et al., 2018; Q. Hu et al., 2016; Hwang et al., 2017; Lin et al., 2022; Ohtani, 2020; Ohtani & Ishii, 2024; Walter, 2021). While hydrous and nominally anhydrous minerals temporarily store water during slab descent, over two-thirds of subducted water is lost by dehydration reactions before reaching 240 km depth (van Keken et al., 2011). As subducted materials descend into the uppermost lower mantle, the water flux can diminish further. This is driven by the dehydration of hydrous phases such as dense hydrous magnesium silicates (e.g., superhydrous phase B and phase D) and the transition of hydrous ringwoodite around the 660-km discontinuity, resulting in bridgmanite + ferropericlase, which are poor water reservoirs due to its extremely low water solubility (<0.1 wt.%) (Bolfan-Casanova et al., 2002; Duan et al., 2018; Ghosh et al., 2013; Ishii, Criniti, Purevjav, et al., 2024; Ishii, Ohtani, & Shatskiy, 2022; J. Liu et al., 2017; Y. Liu et al., 2021; Z. Liu et al., 2021; Nishi et al., 2014, 2017; Ohtani, 2021; Ohtani et al., 2014). These limit water

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transport into the deeper region, raising a fundamental question: How does the Earth retain and redistribute water at depths beyond 660 km?

Seismological, numerical, and experimental studies suggest that significant amounts of oceanic crust have been subducted into and accumulated in the lower mantle (Ballmer et al., 2015; Ishii, Kojitani & Akaogi, 2019; Kaneshima, 2019). Recently, increasing attention has turned to SiO<sub>2</sub>, the major constituent of the oceanic crust. Upon subduction into the lower mantle, SiO<sub>2</sub> can account for as much as 25 vol.% of the subducted oceanic crust (Irfune & Tsuchiya, 2015; Ishii, Miyajima, et al., 2022). Although nearly pure SiO<sub>2</sub> stishovite is stable in the dry system at top-lower mantle conditions, experimental studies have shown that SiO<sub>2</sub> can accommodate more than 1 wt.% H<sub>2</sub>O together with Al<sub>2</sub>O<sub>3</sub> (Ishii, Criniti, et al., 2022; Litasov et al., 2007). Incorporation of the large amounts of Al and H stabilizes CaCl<sub>2</sub>-type phase, a high-pressure polymorph of stishovite, even under top-lower mantle conditions (Criniti et al., 2023; Ishii, Criniti, et al., 2022; Yu et al., 2025; Y. Zhang et al., 2022). Recent findings suggest that this hydrous CaCl<sub>2</sub>-type aluminous SiO<sub>2</sub> can retain weight percent levels of water in the crystal structure close to the core-mantle boundary conditions, demonstrating exceptional water storage capacity (Tsutsumi et al., 2024). These insights challenge previous assumptions about the slab dehydration limit, positioning (Al, H)-bearing CaCl<sub>2</sub>-type SiO<sub>2</sub> as a key phase in revising our understanding of water cycling in the deep-mantle (Tsutsumi et al., 2024).

Despite its potential significance in deep-water transport, the physical properties of (Al, H)-bearing CaCl<sub>2</sub>-type SiO<sub>2</sub> remain poorly constrained under relevant lower mantle pressure and temperature (*P-T*) conditions. In particular, the structural responses of this phase to Al incorporation, compression, and temperature, which are critical for understanding its stability and elasticity, are not well understood. In this study, we demonstrate that hydrogen-bond symmetrization occurs in (Al, H)-bearing CaCl<sub>2</sub>-type SiO<sub>2</sub> at deep-mantle conditions, leading to a markedly stiffened structure. This conclusion is supported by synchrotron infrared and Raman spectroscopy, combined with X-ray diffraction measurements, which are commonly used to clarify hydrogen-bond symmetrization (Aoki et al., 1996; Goncharov et al., 1999; Hou et al., 2021; Y. Liu et al., 2021; Z. Liu et al., 2021; Struzhkin et al., 1997; Zha et al., 2016). This finding can explain the significant thermal stability of (Al, H)-bearing CaCl<sub>2</sub>-type SiO<sub>2</sub>, emphasizing its importance for a plausible long-term water reservoir in the deep lower mantle.

## 2. Experimental Methods

### 2.1. Sample Preparation and Characterization

Starting samples were prepared by mixing reagent-grade SiO<sub>2</sub> (quartz) and Al(OH)<sub>3</sub> (gibbsite) in molar ratios of 9:1 (run 1K3783) and 17:3 (run 1K3774), respectively. The intentional excess of Al<sub>2</sub>O<sub>3</sub> and H<sub>2</sub>O in the starting materials was designed to synthesize post-stishovite samples with high water contents. The sample assemblage with a LaCrO<sub>3</sub> heater was compressed to 24 GPa and then heated to 2173 K for 2 hr using a 1,000-ton Kawai-type multi-anvil apparatus at the Institute for Planetary Materials (IPM), Okayama University. Detailed procedures for sample synthesis and characterization have been previously reported (Ishii, Criniti, et al., 2022; X. Zhang et al., 2025).

The chemical compositions of the synthesized hydrated Al-bearing CaCl<sub>2</sub>-type SiO<sub>2</sub> samples were determined to be Si<sub>0.929(1)</sub>Al<sub>0.071(1)</sub>O<sub>2</sub>H<sub>0.033(4)</sub> (run 1K3783) and Si<sub>0.898(2)</sub>Al<sub>0.102(3)</sub>O<sub>2</sub>H<sub>0.064(5)</sub> (run 1K3774), using a JXA-8530F Plus electron microprobe with 15 kV and 10 nA at the Key Laboratory of Crust-Mantle Materials and Environments, University of Science and Technology of China (USTC). Therein, the hydrogen (H) content was estimated based on the H:Al ratio derived from nuclear magnetic resonance measurements (Text S1 and Figure S1a in Supporting Information S1). For simplicity, these compositions are abbreviated as (Al<sub>7.1</sub>, H<sub>3.3</sub>)-SiO<sub>2</sub> and (Al<sub>10.2</sub>, H<sub>6.4</sub>)-SiO<sub>2</sub>, respectively. The analyses of single-crystal XRD spectra of synthesized crystals confirmed that both (Al<sub>7.1</sub>, H<sub>3.3</sub>)-SiO<sub>2</sub> and (Al<sub>10.2</sub>, H<sub>6.4</sub>)-SiO<sub>2</sub> samples adopt an orthorhombic structure with *Pnnm* space group at ambient conditions, corresponding to a CaCl<sub>2</sub>-type SiO<sub>2</sub> (post-stishovite) (Text S2 in Supporting Information S1 for more details).

### 2.2. High Pressure Single-Crystal Synchrotron Infrared Spectroscopy Experiments

High-pressure infrared spectroscopy measurements were conducted at the infrared beamline BL01B of the National Synchrotron Radiation Laboratory (NSRL) at the upgraded Hefei Light Source (HLS-II, Hefei, China). The

synchrotron beam energy was 0.8 GeV. The experimental setup included a Bruker Vertex 70v FT-IR spectrometer (Bruker Corporation, Germany) coupled with a Hyperion 3,000 microscope (Bruker Corporation, Germany). The system was equipped with a KBr beam-splitter and a liquid nitrogen-cooled MCT-A detector, providing an infrared spectral resolution of  $4\text{ cm}^{-1}$  (C. Hu et al., 2020).

The single-crystal samples of  $(\text{Al}_{7.1}, \text{H}_{3.3})\text{-SiO}_2$  and  $(\text{Al}_{10.2}, \text{H}_{6.4})\text{-SiO}_2$  were double-polished to a thickness of  $10\text{--}14\text{ }\mu\text{m}$  and cut into  $\sim 40 \times 30\text{ }\mu\text{m}^2$  in diameter using a hard blade. Each composition was separately loaded into the sample chamber, together with two ruby spheres as the pressure calibrant (Dewaele et al., 2004). Ne was loaded into the sample chamber as a pressure-transmitting medium. Infrared spectra for  $(\text{Al}_{7.1}, \text{H}_{3.3})\text{-SiO}_2$  and  $(\text{Al}_{10.2}, \text{H}_{6.4})\text{-SiO}_2$  were measured at high pressure up to 47 GPa and 300 K. The aperture size was set to  $20 \times 20\text{ }\mu\text{m}^2$ , and background spectra were measured through the diamond anvils within the Ne-filled gasket hole.

### 2.3. High Temperature and/or High Pressure Raman Spectroscopy Experiments

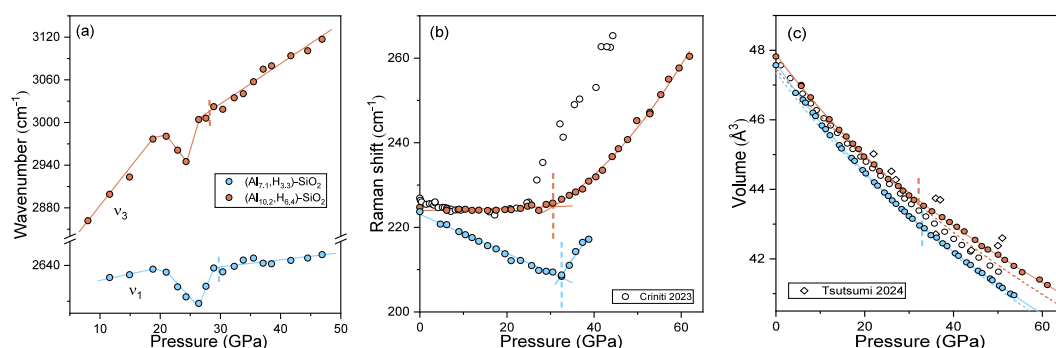
Diamond anvils with 300 or 400  $\mu\text{m}$  flat culets were used to achieve high pressures. A pre-indented rhenium gasket with a thickness of  $\sim 30\text{--}50\text{ }\mu\text{m}$  was drilled by a laser drilling machine in the center with a diameter of  $180\text{--}240\text{ }\mu\text{m}$  and used as the sample chamber. Two single-crystal samples,  $(\text{Al}_{7.1}, \text{H}_{3.3})\text{-SiO}_2$  and  $(\text{Al}_{10.2}, \text{H}_{6.4})\text{-SiO}_2$ , were double-polished to a thickness of  $10\text{--}14\text{ }\mu\text{m}$  and cut to  $\sim 40 \times 30\text{ }\mu\text{m}^2$  in diameter. Each composition sample was loaded into the chamber, together with 1–2 ruby spheres and/or some  $\text{SrB}_4\text{O}_7\text{:Sm}^{2+}$  powder as pressure calibrants (Datchi et al., 2007; Dewaele et al., 2004). The Ne was used as a pressure-transmitting medium.

During the high  $P$ - $T$  experiments, the sample chamber was uniformly heated using a surrounding resistive furnace. Temperature was measured with a K-type thermocouple (Omega Technology Company). Raman spectra of samples were recorded using a Renishaw RM1000 micro-confocal laser Raman spectrometer. Fluorescence spectra of ruby and  $\text{SrB}_4\text{O}_7\text{:Sm}^{2+}$  were measured in the range from 675 to 730 nm at high pressure and/or high temperature conditions. Pressure was determined by multiple fluorescence measurements of ruby at 300 K and  $\text{SrB}_4\text{O}_7\text{:Sm}^{2+}$  powder at 500–800 K both before and after each Raman spectrum acquisition (Datchi et al., 2007; Dewaele et al., 2004). The singlet nature of the  $^5\text{D}_0\text{--}^7\text{F}_0$  line persists at entire  $P$ - $T$  range (Figure S2 in Supporting Information S1). Raman spectra of single-crystal hydrated Al-bearing  $\text{SiO}_2$  were collected under high  $P$ - $T$  conditions, reaching up to 62 GPa and 800 K, covering frequencies ranging from 100 to  $1,000\text{ cm}^{-1}$ . Four independent experimental runs were conducted at high temperatures of 300, 500, 650, and 800 K under high pressure conditions. Raman spectrum fitting was conducted using PeakFit v4.12 software. Additional details of the experimental procedures have been reported elsewhere (Zhao et al., 2024).

### 2.4. High Pressure Synchrotron Single-Crystal XRD Experiments

High-pressure XRD measurements of  $(\text{Al}_{10.2}, \text{H}_{6.4})\text{-SiO}_2$  sample were performed at the Extreme Conditions Beamline P02.2 of PETRA III (DESY, Hamburg, Germany). The experiments utilized an  $8 \times 3\text{ }\mu\text{m}^2$  X-ray beam at 42.7 keV ( $\lambda = 0.2910\text{ }\text{\AA}$ ) and a Perkin-Elmer XRD 1621 flat panel detector (Liermann et al., 2015). The other composition  $(\text{Al}_{7.1}, \text{H}_{3.3})\text{-SiO}_2$  was performed at the BL17UM beamline (SSRF, Shanghai, China), utilized a  $5 \times 3\text{ }\mu\text{m}^2$  X-ray beam at 25.65 keV ( $\lambda = 0.4834\text{ }\text{\AA}$ ) and an EIGER2 X-16M flat panel detector. Polycrystalline  $\text{CeO}_2$  (NIST SRM 674b) was used to calibrate the sample-detector distance and instrument parameters for single-crystal XRD, respectively.

High pressures were generated using a pair of 300  $\mu\text{m}$  flat culets. A pre-indented rhenium gasket with a thickness of  $\sim 30\text{ }\mu\text{m}$  was drilled by a laser drilling machine in the center with a diameter of  $180\text{ }\mu\text{m}$  and used as the sample chamber. Two single-crystal  $(\text{Al}_{7.1}, \text{H}_{3.3})\text{-SiO}_2$  and  $(\text{Al}_{10.2}, \text{H}_{6.4})\text{-SiO}_2$  samples were separately double-polished with a thickness of  $8\text{--}12\text{ }\mu\text{m}$  and cut into  $\sim 40 \times 30\text{ }\mu\text{m}^2$  using a hard blade. Each composition with two different crystal orientations was loaded into the chamber, together with a small piece of Pt plate as a pressure calibrant (Fei et al., 2007). The Ne was used as a pressure-transmitting medium. Pressures were increased up to 62 GPa for  $(\text{Al}_{7.1}, \text{H}_{3.3})\text{-SiO}_2$  and  $(\text{Al}_{10.2}, \text{H}_{6.4})\text{-SiO}_2$ , respectively, using a gas-driven membrane with pressure increments of 1–2 GPa. At each pressure, step scans were acquired upon continuous rotation of the DAC from  $-20^\circ$  to  $+20^\circ$ . The collected XRD data were integrated into 1D patterns and subsequently analyzed by using DIOPAS software (Prescher & Prakapenka, 2015).



**Figure 1.** Hydrogen-bond symmetrization of (Al, H)-bearing  $\text{CaCl}_2$ -type  $\text{SiO}_2$  at high pressure and 300 K. (a) Wavenumber of OH mode from IR measurements. (b) Raman shifts of the  $A_{1g}$  mode. (c) Pressure-Volume relationship for  $(\text{Al}_{7.1}, \text{H}_{3.3})\text{-SiO}_2$  (orange circles) and  $(\text{Al}_{10.2}, \text{H}_{6.4})\text{-SiO}_2$  (blue circles) at 300 K. The dashed orange and blue lines: the onset phase transition of hydrogen-bond symmetrization states for  $(\text{Al}_{7.1}, \text{H}_{3.3})\text{-SiO}_2$  and  $(\text{Al}_{10.2}, \text{H}_{6.4})\text{-SiO}_2$ , respectively, this study; open squares: Raman shifts of the  $A_{1g}$  mode and volumes at high pressure for  $(\text{Al}_{10.6}, \text{H}_{7.2})\text{-SiO}_2$  from reference (Criniti et al., 2023); open diamonds: volume at high pressure for  $\text{CaCl}_2$ -type  $\text{SiO}_2$  from reference (Tsutsumi et al., 2024). The error bar is within the symbol and not shown for clarity.

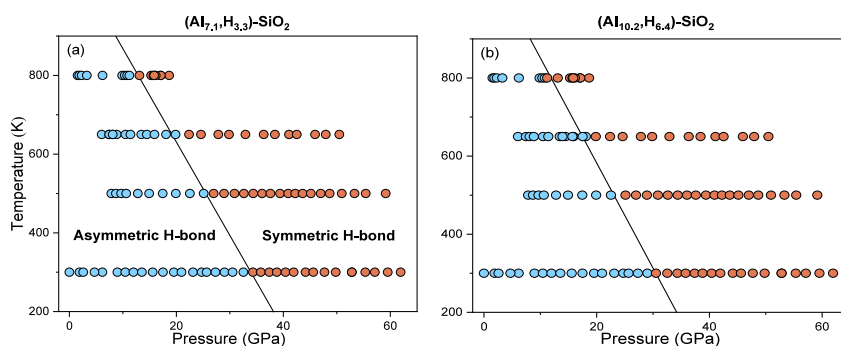
### 3. Results and Discussion

#### 3.1. Hydrogen-Bond Symmetrization Stiffens (Al, H)-Bearing $\text{SiO}_2$

Synchrotron infrared spectroscopy experiments were conducted on two representative single-crystal (Al, H)-bearing  $\text{CaCl}_2$ -type  $\text{SiO}_2$ ,  $(\text{Al}_{7.1}, \text{H}_{3.3})\text{-SiO}_2$  and  $(\text{Al}_{10.2}, \text{H}_{6.4})\text{-SiO}_2$ , at high pressures ranging from 8 to 47 GPa at 300 K (Figure 1a; Figure S3 in Supporting Information S1). Multiple OH stretching modes were detected in our infrared spectra. In particular, both the  $\nu_1$  OH stretching mode of  $(\text{Al}_{7.1}, \text{H}_{3.3})\text{-SiO}_2$  and the  $\nu_3$  mode of  $(\text{Al}_{10.2}, \text{H}_{6.4})\text{-SiO}_2$  display a sharp wavenumber decrease before the transition, accompanied by a clear inflection in its pressure-dependent slope ( $d\nu/dP$ ) at the phase boundary. The abrupt inflection in the pressure evolution of this region is characteristic of O-H bond reorientation, which reveals a transition from ordered to disordered hydrogen in (Al, H)-bearing  $\text{CaCl}_2$ -type  $\text{SiO}_2$  prior to hydrogen-bond symmetrization (Figure S4 in Supporting Information S1), analogous to transitions observed in other hydrous minerals, such as phase Egg and  $\delta\text{-AlOOH}$  (Hou et al., 2021; Kagi et al., 2010; Y. Liu et al., 2021; Z. Liu et al., 2021; Meier et al., 2022; Ohira et al., 2019; Sano-Furukawa et al., 2018; Thompson et al., 2020; Yan et al., 2025). Subsequently, the wavenumbers of these two OH modes increase monotonically again at  $\sim 30$  GPa for  $(\text{Al}_{7.1}, \text{H}_{3.3})\text{-SiO}_2$  and  $\sim 28$  GPa for  $(\text{Al}_{10.2}, \text{H}_{6.4})\text{-SiO}_2$ , indicating the transition from disordered hydrogen to the hydrogen-bond symmetrization state in  $\text{CaCl}_2$ -type  $\text{SiO}_2$  (Figure 1a; Table S1 in Supporting Information S1). Both (Al, H)-bearing  $\text{CaCl}_2$ -type  $\text{SiO}_2$  and phase egg undergo phase transitions from an ordered to a disordered hydrogen state, eventually reaching a hydrogen-bond symmetrization state (Y. Liu et al., 2021; Z. Liu et al., 2021). Notably, the pressure dependence of the OH-stretching wavenumber in (Al, H)-bearing  $\text{CaCl}_2$ -type  $\text{SiO}_2$  exhibits an opposite trend to that in phase egg, which is attributed to their structural differences. In (Al, H)-bearing  $\text{CaCl}_2$ -type  $\text{SiO}_2$ , pressure enhances orthorhombic distortion through tilting of  $(\text{Si,Al})\text{O}_6$  octahedra, triggering hydrogen-bond symmetrization and strengthening the O-H bond (Panero & Stixrude, 2004; Tsutsumi et al., 2024). In contrast, in the phase egg, which consists of corner-sharing  $\text{AlO}_6\text{-(SiO}_6)_2\text{-AlO}_6$  octahedra units that effectively isolate hydrogen, the O-H bond elongates with increasing pressure, as confirmed by experimental study and theory calculations (Y. Liu et al., 2021; Z. Liu et al., 2021; Mookherjee et al., 2019).

Moreover, the  $\nu_2$  and  $\nu_4$  OH stretching modes on  $(\text{Al}_{7.1}, \text{H}_{3.3})\text{-SiO}_2$ , and the  $\nu_1$ ,  $\nu_2$ ,  $\nu_5$ , and  $\nu_6$  modes on  $(\text{Al}_{10.2}, \text{H}_{6.4})\text{-SiO}_2$  also show a clear slope changes ( $d\nu/dP$ ) across the symmetrization boundary (Figure S3 in Supporting Information S1), as reported in hydrous minerals (Hou et al., 2021; Kagi et al., 2010; Y. Liu et al., 2021; Z. Liu et al., 2021; Meier et al., 2022; Ohira et al., 2019; Sano-Furukawa et al., 2018; Thompson et al., 2020; Yan et al., 2025). These observations further support our findings.

In (Al, H)-bearing  $\text{CaCl}_2$ -type  $\text{SiO}_2$ , similar anomalous behavior is observed in the  $A_{1g}$  Raman mode over the same pressure range as the synchrotron infrared anomalies. In  $(\text{Al}_{7.1}, \text{H}_{3.3})\text{-SiO}_2$ , the  $A_{1g}$  mode first softens with increasing pressure up to  $\sim 33$  GPa, and then reverses to a hardening trend at higher pressures (Figure 1b; Figure



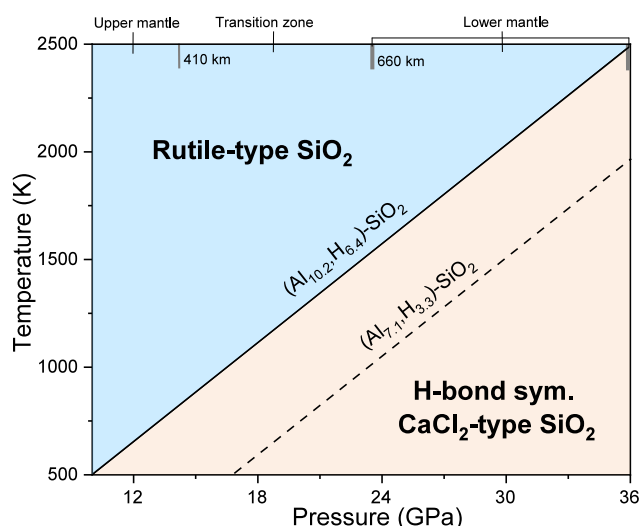
**Figure 2.** Phase diagram of hydrogen-bond symmetrization in (Al, H)-bearing  $\text{CaCl}_2$ -type  $\text{SiO}_2$ . (a)  $(\text{Al}_{7.1}, \text{H}_{3.3})\text{-SiO}_2$ ; (b)  $(\text{Al}_{10.2}, \text{H}_{6.4})\text{-SiO}_2$ . The solid lines are phase boundary showing the transition from asymmetric (blue circles) to symmetric (orange circles) hydrogen-bond in (Al, H)-bearing  $\text{CaCl}_2$ -type  $\text{SiO}_2$ . The error bar is within the symbol and not shown for clarity.

S5 and Tables S2–S3 in Supporting Information S1). A reversed pressure dependence of the Raman shift of OH-stretching mode was observed in  $\text{FeOOH}_x$  and  $\text{H}_2\text{O}$ , which is attributed to hydrogen-bond symmetrization (Hou et al., 2021; Zha et al., 2016). Therefore, this anomalous behavior in  $(\text{Al}_{7.1}, \text{H}_{3.3})\text{-SiO}_2$  reflects a pressure-induced shift from asymmetric to symmetric hydrogen bonds, which shortens the O–H···O distance and stiffens the Si–O framework. A similar transition occurs in  $(\text{Al}_{10.2}, \text{H}_{6.4})\text{-SiO}_2$ , where the  $A_{1g}$  mode remains nearly pressure-invariant below ~30 GPa and then stiffens abruptly, indicating a lower transition pressure at higher Al and H contents. In contrast, the  $B_{2g}$  and  $A_{2g}$  modes of both compositions increase monotonically across the entire pressure range, being unaffected by the hydrogen-bond geometry. These Raman features closely mirror the IR spectral changes, reinforcing the interpretation of a pressure-induced hydrogen-bond symmetrization. Although the O–H stretching vibration is not directly probed by Raman spectroscopy, the anomalies in  $A_{1g}$  Raman mode can be considered as indicators of the hydrogen-bond symmetrization transition.

Synchrotron single-crystal XRD reveals that hydrogen-bond symmetrization markedly enhances the incompressibility of  $\text{CaCl}_2$ -type  $\text{SiO}_2$  phase. An obvious change in the slopes of the pressure-volume relationship is detected at ~33 GPa for  $(\text{Al}_{7.1}, \text{H}_{3.3})\text{-SiO}_2$  and ~32 GPa for  $(\text{Al}_{10.2}, \text{H}_{6.4})\text{-SiO}_2$ , indicating a change in the compressibility mechanism of (Al, H)-bearing  $\text{CaCl}_2$ -type  $\text{SiO}_2$  (Figure 1c; Figures S6, S7, Tables S4 and S5 in Supporting Information S1). This change is attributed to hydrogen-bond symmetrization, in which hydrogen atoms relocate to central symmetric positions, forming strengthened O–H···O linkages that stiffen the Si–O framework (Ishii, Criniti, et al., 2022; Tsutsumi et al., 2024) (Figure S4 in Supporting Information S1). Similar slope changes in pressure-volume data have been reported in other hydrous minerals (e.g., phase egg, phase D,  $\delta\text{-(Al,Fe)OOH}$ ) and are associated with hydrogen-bond symmetrization (Hushur et al., 2011; Y. Liu et al., 2021; Z. Liu et al., 2021; Ohira et al., 2019; Sano-Furukawa et al., 2009; Su et al., 2021). The  $P$ - $V$  data were fitted by the second-order Birch-Murnaghan equation of state with the fixed pressure derivative of 4, yielding a bulk modulus ( $K_0$ ) increase from 255 to 276 GPa (8%) for  $(\text{Al}_{7.1}, \text{H}_{3.3})\text{-SiO}_2$  and from 283 to 329 GPa (16%) for  $(\text{Al}_{10.2}, \text{H}_{6.4})\text{-SiO}_2$  across the transition. These consistent increases in  $K_0$  across compositions confirm that hydrogen-bond symmetrization leads to a crystallographically more rigid and less compressible  $\text{CaCl}_2$ -type  $\text{SiO}_2$ . The transition pressures derived from XRD are in agreement, within experimental uncertainty, with those determined by infrared and Raman spectroscopy, providing converging evidence for the formation of the hydrogen-bond symmetrized state (Table S6 in Supporting Information S1). It is noteworthy that neon was employed as a pressure-transmitting medium in all infrared, Raman, and XRD experiments, and its standard deviation pressure is only 0.2 GPa at ~30 GPa, corresponding to the phase transition pressure of hydrogen-bond symmetrization, which eliminates the influence of non-hydrostaticity (Klotz et al., 2009).

### 3.2. Temperature-Driven Early Onset of Hydrogen-Bond Symmetrization

Our high  $P$ - $T$  Raman measurements reveal a pronounced temperature dependence for the hydrogen-bond symmetrization transition in (Al, H)-bearing  $\text{CaCl}_2$ -type  $\text{SiO}_2$  (Figure 2). As the temperature increases, the transition pressure decreases sharply for both compositions examined. The transition is identified by a reversal in the pressure dependence of the  $A_{1g}$  Raman mode, consistent with the signature observed at 300 K (Figures S5, S8 and



**Figure 3.** Phase transition of  $\text{SiO}_2$  at mantle conditions. The solid and dashed black lines are the phase boundary from rutile-type  $\text{SiO}_2$  to hydrogen-bond symmetrization in (Al, H)-bearing  $\text{CaCl}_2$ -type  $\text{SiO}_2$  for  $(\text{Al}_{10.2}, \text{H}_{6.4})\text{-SiO}_2$  and  $(\text{Al}_{7.1}, \text{H}_{3.3})\text{-SiO}_2$ , respectively. The incorporation of Al and H substantially lowers the phase transition pressure from rutile-type to the  $\text{CaCl}_2$ -type structure.

S9 in Supporting Information S1). In  $(\text{Al}_{7.1}, \text{H}_{3.3})\text{-SiO}_2$ , the transition pressure drops from  $\sim 33$  GPa at 300 K to  $\sim 12$  GPa at 800 K. Similarly,  $(\text{Al}_{10.2}, \text{H}_{6.4})\text{-SiO}_2$  undergoes the transition at a relatively low pressure of  $\sim 11$  GPa at 800 K, compared to  $\sim 30$  GPa at 300 K. These results correspond to negative Clapeyron slopes of  $-23.8(23)$  K/GPa for  $(\text{Al}_{7.1}, \text{H}_{3.3})\text{-SiO}_2$  and  $-26.7(28)$  K/GPa for  $(\text{Al}_{10.2}, \text{H}_{6.4})\text{-SiO}_2$  (Figure 2), reflecting the strong thermal sensitivity of hydrogen mobility and negligible compositional effect.

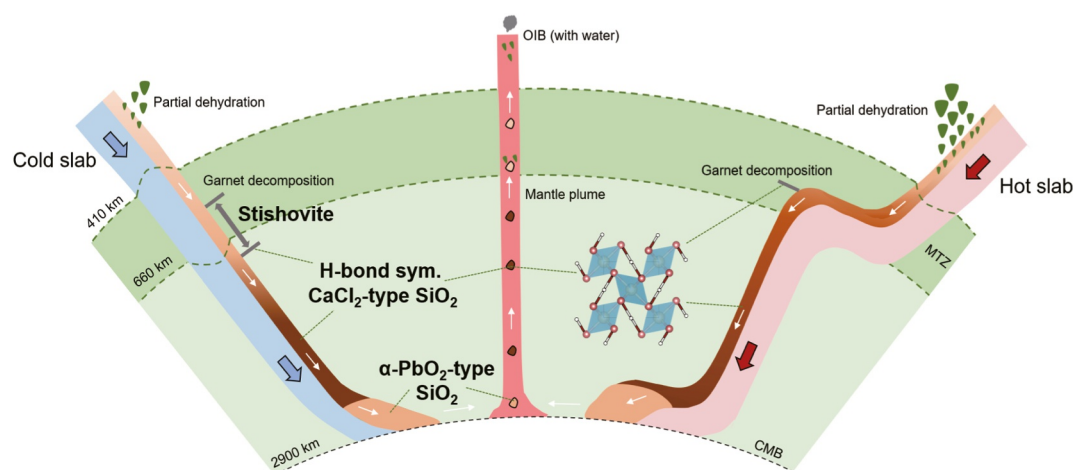
Elevated temperatures promote dynamic reorientation of hydrogen atoms, reducing kinetic barriers and allowing hydrogen-bond symmetrization to occur at significantly lower pressures (Umemoto et al., 2016). Notably, under typical mantle temperatures, this implies that once (Al, H)-bearing  $\text{CaCl}_2$ -type  $\text{SiO}_2$  forms from rutile-type precursors (stishovite), it likely exists in a hydrogen-bond symmetrized state in the deep-mantle (Figure 3; Text S3 in Supporting Information S1). Subsequently, the hydrogen-bond symmetrized state in (Al, H)-bearing  $\text{CaCl}_2$ -type  $\text{SiO}_2$  may further evolve into a superionic state under elevated  $P$ - $T$  conditions based on molecular dynamics simulations and electrical conductivity measurements (Inada et al., 2025; Umemoto et al., 2016) (Figure S10 in Supporting Information S1). Similar phase transitions from hydrogen-bond symmetrization to superionic state have also been reported in  $\text{H}_2\text{O}$  and  $\delta\text{-AlOOH}$  (Aoki et al., 1996; Goncharov et al., 1999; He et al., 2026; Hou et al., 2021; Ohira et al., 2019; Prakapenka et al., 2021; Sano-Furukawa et al., 2018; Struzhkin et al., 1997; Zha et al., 2016). These thermally activated transitions thus represent a critical

shift in the stability and transport properties of water in deep Earth environments (He et al., 2026; Hou et al., 2021; Tsuchiya, 2024).

#### 4. Geophysical Implications

The dehydration of hydrous phases could release substantial amounts of water into the topmost lower mantle when the subducting slab becomes warm enough to destabilize them (Nishi et al., 2014; Ohtani, 2021). Although dominant lower mantle minerals such as bridgmanite and ferropericlase have limited water storage capacities (Bolfan-Casanova et al., 2002; Y. Liu et al., 2021; Z. Liu et al., 2021; Ohtani, 2021), liebermannite, stishovite, and majorite in a sediment or continental crust on the basalt layer can temporarily capture the released water together at the bottom of the transition zone and topmost lower mantle (Irfune et al., 1994; Manthilake et al., 2020). However, given that the density of liebermannite-bearing subducted slabs is lower than that of the surrounding mantle below 660 km depth, such slabs might be gravitationally unstable at these depths (Nishiyama et al., 2005). Meanwhile, majoritic garnet undergoes decomposition and releases  $\text{Al}_2\text{O}_3$  at the bottom of the transition zone and topmost lower mantle (Marquardt & Thomson, 2020; Nishiyama et al., 2005). Ultimately, the released water and  $\text{Al}_2\text{O}_3$  are expected to be partially incorporated into stishovite, due to its high stability and abundance, which would form hydrogen-bond symmetrized  $\text{CaCl}_2$ -type (Al, H)-bearing  $\text{SiO}_2$  (Figure 4). Even within cold subducting slabs, hydrous phases would dehydrate at greater depths (Chen et al., 2025), causing the delayed transition from stishovite to the  $\text{CaCl}_2$ -type  $\text{SiO}_2$  phase. Once this transition occurs, the resulting (Al, H)-bearing  $\text{CaCl}_2$ -type  $\text{SiO}_2$  immediately adopts a hydrogen-bond symmetrized structure.

Hydrogen-bond symmetrization plays a key role in stabilizing (Al, H)-bearing  $\text{CaCl}_2$ -type  $\text{SiO}_2$  in the lower mantle. Previous studies reported that the water storage capacity of  $\text{CaCl}_2$ -type  $\text{SiO}_2$  increases from  $\sim 1.1$  wt.% near the top of the lower mantle to  $\sim 3.6$  wt.% approaching the core-mantle boundary (Ishii, Criniti, et al., 2022; Tsutsumi et al., 2024). Our results explain this depth-dependent trend by linking it to pressure-enhanced orthorhombic distortion, which is reflected in increasing  $a/b$  axial ratios and caused by the tilting of  $(\text{Si,Al})\text{O}_6$  octahedra (Figure S11 in Supporting Information S1) (Ishii, Criniti, et al., 2022; Panero & Stixrude, 2004; Tsutsumi et al., 2024; Umemoto et al., 2016). This distortion shortens oxygen-oxygen distances within hydrogen bonds, triggering hydrogen-bond symmetrization that strengthens the bonds and further stabilizes the crystal structure, thereby enabling greater water incorporation at greater depths (Figure S4 in Supporting Information S1) (Meier et al., 2022; Sano-Furukawa et al., 2009, 2018; Thompson et al., 2017; Tsuchiya, 2024; Tsuchiya et al., 2005). Infrared spectroscopy supports this interpretation, showing systematic blue-shifts in OH stretching



**Figure 4.** Schematic representation of water transportation in the lower mantle. Decomposition of garnet significantly increases the  $\text{SiO}_2$  content in the subducted oceanic crust within the mantle transition zone. In hot subducting slabs, dehydration of Al-bearing hydrous phases occurs in the transition zone, releasing Al and H that can be incorporated into  $\text{SiO}_2$  and stabilize hydrogen-bond symmetrized  $\text{CaCl}_2$ -type  $\text{SiO}_2$  even at the base of the transition zone. In cold slabs, this symmetrized  $\text{CaCl}_2$ -type  $\text{SiO}_2$  forms at greater depths through the phase transition from stishovite due to persistence of hydrous minerals at relatively low temperatures. The resulting stiff and hydrogen-bond symmetrized  $\text{CaCl}_2$ -type  $\text{SiO}_2$  serves as a major carrier for transporting water into the lower mantle. Meanwhile, hydrogen-bond symmetrized  $\text{CaCl}_2$ -type  $\text{SiO}_2$  can return to the shallow Earth via upwelling mantle plumes. Back transition to stishovite may release water to the surrounding mantle and explain a higher water content in ocean island basalts.

modes under compression, confirming progressive hydrogen-bond stabilization (Figure 1a). Moreover, recent experiments show that even at lower mantle pressures and temperatures exceeding 3000 K,  $\text{CaCl}_2$ -type  $\text{SiO}_2$  can retain significant amounts of water while coexisting with silicate melt (Tsutsumi et al., 2024). This suggests that the transition from hydrogen-bond symmetrization to superionic hydrogen further dramatically enhances the water-retention capacity of  $\text{SiO}_2$ , effectively locking hydrogen within the crystal structure and preventing its escape into the melt. Consequently, subducted oceanic crusts may not undergo large-scale dehydration in the lower mantle, instead, water can be transported to the bottom of the lower mantle via hydrogen-bond symmetrization and superionic hydrogen in (Al, H)-bearing  $\text{CaCl}_2$ -type  $\text{SiO}_2$  (Figure 4; Figure S10 in Supporting Information S1) (Inada et al., 2025; Tsutsumi et al., 2024; Umemoto et al., 2016). When the phase transition to the  $\alpha$ - $\text{PbO}_2$ -type structure happens near the core-mantle boundary (Tsutsumi et al., 2024), it is plausible that this phase hosts hydrogen-bond symmetrization or superionic hydrogen, thereby allowing water to remain trapped in  $\alpha$ - $\text{PbO}_2$ -type  $\text{SiO}_2$  even in the presence of melt. Of course, hydrogen-bond symmetrization or superionic hydrogen in  $\alpha$ - $\text{PbO}_2$ -type  $\text{SiO}_2$  remains to be confirmed by future experiments.

These findings underscore a previously underappreciated mechanism by which water can be efficiently stabilized and transported through the lower mantle. The formation of hydrogen-bond symmetrized (Al, H)-bearing  $\text{CaCl}_2$ -type  $\text{SiO}_2$  under realistic subduction conditions, facilitated by Al and H incorporation, not only resolves the paradox of water retention in nominally anhydrous minerals, but also establishes  $\text{SiO}_2$  as a robust deep-water carrier. Its remarkable ability to preserve water fundamentally reshapes our understanding of the deep Earth's water cycle. If hydrogen-bond symmetrization or superionic hydrogen persists in the  $\alpha$ - $\text{PbO}_2$ -type phase at the core-mantle boundary, as our results suggest, this could represent a long-term reservoir for water at Earth's deepest interior, effectively linking surface water transportation to deep-mantle and core-mantle boundary processes.

Based on current subduction parameters (global rate: 5 cm/year, length of subduction zones: 46,000 km, crustal thickness: 6 km), we estimate that approximately  $8 \times 10^{22}$  kg of oceanic crust has been subducted over geological time ( $4 \times 10^9$  years) (Panero et al., 2003; van Keken et al., 2011). This corresponds to  $2 \times 10^{22}$  kg of stishovite, which makes up about 25 vol.% of the high-pressure MORB assemblage. Given that slower rates of 1–3 cm/year are plausible for slabs descending into the lower mantle due to the significantly increase of mantle viscosity (Goes et al., 2017; Li et al., 2024; Marquardt & Miyagi, 2015). This would promote slab thickening, and ultimately lower the efficiency of deep-water transport. Based on the water capacity in hydrogen-bond symmetrization,

superionic state of (Al, H)-bearing  $\text{CaCl}_2$ -type  $\text{SiO}_2$  and  $\alpha$ - $\text{PbO}_2$ -type phase is 1.1 wt.%, 3.6 wt.%, and 2.0 wt.%, respectively (Ishii, Criniti, et al., 2022; Tsutsumi et al., 2024). If we adopt a subduction rate of 2 cm/year for slabs descending into the lower mantle during deep-water cycle, it means that about  $4.4 \times 10^{19}$  kg of water can be retained in hydrogen-bond symmetrization of (Al, H)-bearing  $\text{CaCl}_2$ -type  $\text{SiO}_2$  phase and about  $2.9 \times 10^{19}$  kg of water in superionic state of (Al, H)-bearing  $\text{CaCl}_2$ -type  $\text{SiO}_2$  transported into the bottom of the lower mantle. Ultimately, about  $1.6 \times 10^{20}$  kg of water in the  $\alpha$ - $\text{PbO}_2$ -type phase may accumulate at the core-mantle boundary, potentially forming localized aqueous reservoirs through geological time.

Moreover, the accumulation of high electrical conductivity and low velocity properties of (Al, H)-bearing  $\text{SiO}_2$  could provide a plausible explanation for the observed high geomagnetic anomalies in the mid-mantle and seismic anomalies in large low shear velocity provinces (Inada et al., 2025; Krymaris et al., 2025; T. Liu et al., 2024). Meanwhile, seismic scatterers with  $\sim 10$ -km thick and low shear-wave velocity anomalies have been widely observed down to the mid-lower mantle, particularly in regions near subducting slabs, and are commonly interpreted as fragments of subducted oceanic crusts (Kaneshima, 2019; Ohtani & Ishii, 2024). Similar scatterers have also been identified in upwelling hot plumes at mid-mantle depths beneath Samoan hotspots (Kaneshima, 2023). Owing to its exceptional water retention, hydrogen-bond symmetrized or superionic hydrogen (Al, H)-bearing  $\text{CaCl}_2$ -type  $\text{SiO}_2$  may facilitate the return of water from the lowermost mantle to shallower depths via plume ascent (Figure 4). It may finally dehydrate and back-transform to (Al, H)-poor stishovite (Ishii, Criniti, et al., 2022; Litasov et al., 2007; Ohtani & Ishii, 2024), releasing water to the surrounding mantle. Geochemical observations showed that ocean island basalts have much higher water contents than mid-ocean ridge basalts (Hirschmann, 2006). This observation can be explained by water dehydrated from hydrogen-bond symmetrized (Al, H)-bearing  $\text{CaCl}_2$ -type  $\text{SiO}_2$ , further emphasizing the key role of (Al, H)-bearing  $\text{CaCl}_2$ -type  $\text{SiO}_2$  on water cycling in the whole mantle.

## Conflict of Interest

The authors declare no conflicts of interest relevant to this study.

## Availability Statement

The data used in this study have been deposited at Zhao et al. (2026).

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## Acknowledgments

We thank Yuzhu Wang and Xinyang Li for high pressure XRD experiment; Tingting Xiao and Wancai Li for EPMA measurement; Hengjie Liu for synchrotron infrared spectra experiments; Yu Ye for Raman data discussion. We acknowledge Yan Wang and Heping Li for providing  $\text{SrB}_4\text{O}_7$ :  $\text{Sm}^{2+}$  powder. We appreciate the two anonymous reviewers for their constructive suggestions and comments, which significantly improved the manuscript. We also thank Editor Quentin Williams for handling our manuscript. This work was funded by National Science Foundation of China (42425202 and 42488101), National Key R&D Program of China (2023YFF0803200), Fundamental Research Funds for the Central Universities (WK2080000207), and the Japan Society for the Promotion of Science KAKENHI Grants (23K19067 and 24K00735). The synthesis of hydrated Al-bearing post-stishovite was fulfilled under the Joint Use/Research Center for “Planetary Materials Sciences,” Institute for Planetary Materials (IPM), Okayama University (Proposal no. I23-008). This work was partially carried out at ECB P02.2 at PETRA-III (DESY) and BL17UM (31124.02.SSRF.BL17UM) at the Shanghai Synchrotron Radiation Facility (proposal: 2024-SSRF-PT-506102 and 2025-SSRF-HZ-511166) and high-pressure synergetic measurement station of Synergic Extreme Condition User Facility. We acknowledge DESY (Hamburg, Germany), a member of the Helmholtz Association HGF, for the provision of experimental facilities.

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