

Superhydrous aluminous silica phases as major water hosts in high-temperature lower mantle^{HPSTAR}₁₅₈₇₋₂₀₂₂

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Water transported by subducted oceanic plates changes mineral and rock properties at high pressures and temperatures, affecting the dynamics and evolution of the Earth's interior. Although geochemical observations imply that water should be stored in the lower mantle, the limited amounts of water incorporation in pyrolitic lower-mantle minerals suggest that water in the lower mantle may be stored in the basaltic fragments of subducted slabs. Here, we performed multianvil experiments to investigate the stability and water solubility of aluminous stishovite and CaCl2-structured silica, referred to as poststishovite, in the SiO2-Al2O3-H2O systems at 24 to 28 GPa and 1,000 to 2,000 °C, representing the pressure-temperature conditions of cold subducting slabs to hot upwelling plumes in the top lower mantle. The results indicate that both alumina and water contents in these silica minerals increase with increasing temperature under hydrous conditions due to the strong Al³⁺-H⁺ charge coupling substitution, resulting in the storage of water up to 1.1 wt %. The increase of water solubility in these hydrous aluminous silica phases at high temperatures is opposite of that of other nominally anhydrous minerals and of the stability of the hydrous minerals. This feature prevents the releasing of water from the subducting slabs and enhances the transport water into the deep lower mantle, allowing significant amounts of water storage in the high-temperature lower mantle and circulating water between the upper mantle and the lower mantle through subduction and plume upwelling. The shallower depths of midmantle seismic scatterers than expected from the pure SiO₂ stishovite-poststishovite transition pressure support this scenario.

poststishovite | upwelling plume | water cycle | lower mantle | subducting slab

Knowing the water solubility of minerals is crucial for understanding the structure and dynamics of the deep mantle because even small amounts of water significantly change the physical and chemical properties of minerals and rocks. For example, water lowers the melting temperature of peridotite to enhance chemical differentiation (1), increases electrical conductivity (2), and decreases creep strength to enhance mantle convection (3). Water is stored in hydrous and nominally anhydrous minerals mainly as hydroxyl groups and hydrous defects, respectively, and is transported into the deep Earth via the subduction of oceanic plates. Since the stability of dense hydrous minerals is generally limited below the average mantle geotherm (4–9), the incorporation of water in nominally anhydrous minerals is of great significance.

Oceanic island basalt contains more water than midocean ridge basalts (10), suggesting water-rich sources in the lower mantle. However, the dominant lower-mantle minerals, bridgmanite and ferropericlase, have limited water solubilities, i.e., <0.1 wt % (11–13). Therefore, not the peridotite layer but the basaltic layer of slabs should mainly transport water. The basaltic rock consists of bridgmanite, davemaoite, CaFe₂O₄-type phase and new hexagonal aluminous phase, and high-pressure silica minerals (14–16). Hence, some of these minerals could have high water solubility.

Among the above-mentioned minerals, high-pressure polymorphs of silica, i.e., stishovite and its $CaCl_2$ -structured modification (poststishovite), are candidates for carrying water into the lower mantle. Some studies actually reported large amounts of water in these silica phases (17, 18). Although they investigated the pure silica phases, the water solubility of stishovite dramatically increases with increasing alumina content, which is the second major component in stishovite and poststishovite (14–16, 19, 20), via the Si⁴⁺ = Al³⁺ + H⁺ charge-coupled substitution (21–24). Therefore, the silica phases in basaltic systems should contain much more water and alumina than considered (21).

Furthermore, it is reported that aluminum incorporation lowers the stishovite-poststishovite transition pressure (24–26). This transition is considered to induce velocity anomalies at around 1,500 km depth (27). Coincidently, seismological studies reported scatterers in the midmantle (28). However, some of these scatterers are located at shallower depths, i.e., 700 to 1,900 km (29), which cannot be explained by the stishovite-poststishovite

Significance

Dense aluminous silica minerals existing in subducted basaltic crusts are among the candidates for carrying water into the deep mantle, but their water solubility is still unclear due to the lack of direct evidence of water incorporation in their crystal structures. We quantitatively clarified that CaCl₂-structured aluminous silica, called poststishovite, can contain weight percent levels of water in its crystal structure under topmost lower-mantle conditions by infrared spectroscopic observations. Our findings suggest that hydrous aluminous poststishovite is stable at lowermantle conditions even in upwelling hot plumes. Owing to its wide pressure-temperature stability field, hydrous aluminous poststishovite plays an important role on the circulation of water between upper and lower mantles within cold subducting slabs and hot upwelling plumes.

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transition in SiO_2 . However, the lowering of the transition pressure by the water-enhanced Al–Si substitution may explain this depth distribution.

To determine the water solubility of aluminous stishovite and poststishovite under topmost lower-mantle conditions, we investigated the phase relations in SiO₂-Al₂O₃-H₂O systems using Kawai-type multianvil apparatus at 24 to 28 GPa and 1,000 to 2,000 °C (Fig. 1). We measured the water contents in recovered aluminous stishovite and poststishovite using Fourier transform infrared (FT-IR) spectroscopy directly showing the OH vibrations. We also conducted two experiments in the SiO₂-Al₂O₃-Fe₂O₃-H₂O system at 24 GPa and 1,700 and 1,900 °C to examine the effect of Fe₂O₃ on the water solubility in aluminous stishovite and poststishovite. The experimental details are described in *Materials and Methods.* The obtained experimental data are given in *SI Appendix,* Tables S1–S7.

High Water Solubility in Poststishovite

A critical finding is that aluminous poststishovite contains vast amounts of water, ranging from 0.85 to 1.1 wt % (Fig. 2). This range is substantially higher than the water solubility of the major lower-mantle minerals, bridgmanite, and ferropericlase (<0.1 wt %) (11–13) as well as aluminous stishovite (0.27 wt %; *SI Appendix*, Tables S1 and S2 and Fig. S4). We thus quantitatively provide evidence of high water contents in silica minerals based on robust measurement using FT-IR spectroscopy.

The water content in poststishovite increases with increasing Al_2O_3 content. The H/Al ratios are lower than but close to unity (Fig. 3 and *SI Appendix*, Table S3) in poststishovite, suggesting that the primary water incorporation mechanism is the charge-coupled substitution of Si⁴⁺ = Al³⁺ + H⁺. Since δ -AlOOH is isostructural with poststishovite (30), this substitution likely corresponds to the formation of the solid solution between poststishovite and δ -AlOOH. In contrast, the H/Al ratios in stishovite are much smaller and close to 1/3. Hence, aluminous stishovite contains large amounts of oxygen vacancies (OV) to compensate for the charge deficiency through the $2Si^{4+} = 2Al^{3+} + OV^{2+}$ substitution.

Despite being isostructural with ε -FeOOH (31, 32), poststishovite obtained from an Fe-bearing starting composition contains only 0.2 to 0.3 wt % of Fe₂O₃ component (*SI Appendix*, Table S2), likely because of the larger ionic radius of V^IFe³⁺ (0.645 Å) than V^ISi⁴⁺ (0.40 Å) (33). However, poststishovite is expected to incorporate more FeOOH at higher pressures, where a high-to-low spin crossover in octahedrally coordinated Fe³⁺ significantly reduces its ionic radius (34–36).

We suggest that the positive temperature dependence of the water solubility in both stishovite and poststishovite is linked to the increasing Al_2O_3 content, which shows a similar temperature dependence. This observation is in striking contrast to other nominally anhydrous minerals such as wadsleyite and ringwoodite, with the negative temperature dependences (37, 38). Although dehydration should occur at higher temperatures in the case of water hosting by other nominally anhydrous minerals, more water incorporation should occur in the case of aluminous stishovite and poststishovite.

The high water content and quenchability of poststishovite might be caused by the formation of strong $Al^{3+} + H^+$ coupling by lattice distortion. As shown in *SI Appendix*, Table S4, the *b* axis is shorter than the *a* axis in poststishovite. The tilting of (Si,Al)O₆ octahedra around the *c* axis causes this shortening of the *b* axis relative to the *a* axis (*SI Appendix*, Fig. S5), which is observed in structural refinements even at ambient conditions

(SI Appendix, Tables S4-S6). As a result, the shortening of O…O distances in the a-b plane (i.e., perpendicular to the c axis) happens (SI Appendix, Fig. S5). The polarized FT-IR spectra of the poststishovite consist of several broad peaks between 2,600 and 3,450 cm⁻¹ (Fig. 2), which can be attributed to the O-H stretching vibration. These peaks display significant anisotropy: the peaks along the a (E/[100]) and b axes (E//[010]) are much more intense than the *c* axis (E//[001]), and that along the *b* axis (E//[010]) is even more intense than the a axis (E//[100]) in poststishovite. The O-H vibrations in poststishovite are therefore considered mainly oriented in the b axis direction, consistently with previous studies and with the orientation of H bonds in δ -AlOOH (39), where the O-H···O bond lies entirely in the *a-b* plane (SI Appendix, Fig. S5). Combining the X-ray diffraction and FT-IR results suggests stabilization of poststishovite due to O-H bonds shortened by the titling of (Si,Al)O₆ octahedra. Thus, these results can provide the reasons that aluminous poststishovite accommodates larger amounts of water than stishovite at topmost lower-mantle conditions and that hydrous aluminous poststishovite can be recovered at ambient condition in contrast to aluminous poststishovite with a smaller water content (26). Although we report the recovery of aluminous poststishovite with Al₂O₃ contents higher than 5.7 wt % at 24 to 28 GPa, stishovite with an Al₂O₃ content of 7.6 wt % was also recovered at relatively low pressure (20 GPa) (21). Despite the high Al₂O₃ content, the aluminous stishovite contained only 0.3 wt % water. This implies that the low water content may be due to a weaker Al-H coupling up to 20 GPa with respect to the synthesis conditions from this study (Fig. 3). The phase change from the hydrous aluminous stishovite to poststishovite observed in this study may be the first-order transition because entropy change could occur and allow hydrogen atoms to redistribute under high pressure and high temperature (40).

Previous studies estimated water contents in SiO₂ stishovite and poststishovite based on their unit cell volume expansion by water incorporation (17, 18) as mentioned above. However, this strategy is not applicable to Al-bearing samples, where the substitution mechanism of H in the stishovite and poststishovite structures is different (21–23). In fact, the volume of hydrous aluminous silica almost linearly changes by incorporation of Al (*SI Appendix*, Figs. S6 and S7), as the ionic radius of V^IAl³⁺ (0.535 Å) is larger than that of ^{VI}Si⁴⁺ (0.40 Å) (33). Therefore, estimating the water content of aluminous silica from volume changes is currently not possible and would require further calibrations using aluminous silica samples of known water content.

Water Transport in the Mantle

Here we provide a scenario of water transport in the deep mantle. Previous studies showed the high water solubility in pure SiO₂ stishovite and discussed the deep water cycle in the lower mantle (17, 18, 41). The current study indicates the tremendously higher water solubility in aluminous poststishovite than in pure SiO₂ stishovite. Al-bearing stishovite is more relevant and appropriate when basaltic layers of slabs are considered, which have a bulk Al₂O₃ content of about 16 wt %. In the hydrous basaltic crust, mineral assemblages of stishovite, bridgmanite, davemaoite, ferropericlase, and a hydrous phase of aluminous phase D or δ -AlOOH are stable at topmost lowermantle depths and cold slab temperatures of 1,000 to 1,200 °C (6). Although no study has investigated the phase relations at higher temperatures, it is likely that the hydrous aluminous



Fig. 1. Phase relations of the stishovite-poststishovite transition in the SiO_2 -Al₂O₃-H₂O system at 24 and 28 GPa. Open and solid circles indicate stishovite (St) and poststishovite (pSt), respectively. Black dashed lines show possible boundaries between St and pSt under high-temperature conditions. The St–pSt transition is assumed to be first order (see text in the section "High Water Solubility in Poststishovite"). The recovered St is assumed to be recovered from high-pressure conditions rather than formed by a back-transformation from pSt. Egg, phase Egg; δ , δ -AlOOH; Cor, corundum.

phases react with stishovite with increasing temperature, and hydrous aluminous poststishovite crystallizes due to the observed $Al^{3+}-H^+$ coupling. Bridgmanite can contain significant amounts of alumina in dry conditions, but the Al concentration was shown to decrease when coexisting with hydrous aluminous phases (42). We can expect a similar behavior when bridgmanite coexists with poststishovite because of the strong $Al^{3+}-H^+$ coupling in poststishovite and the extremely low water solubility in bridgmanite (11–13). Therefore, aluminous silica should play an essential role in water transport to the deep lower mantle. We emphasize the geophysical significance of the higher water solubility in aluminous poststishovite at higher temperatures because this positive temperature dependence prevents the release of water from subducted slabs as they slowly heat up due to thermal equilibration with the hot surrounding mantle.

In the deep upper mantle, subducted slabs transport water as hydrous phases such as δ -AlOOH in basaltic layers (6) and phase A, phase E, superhydrous phase B, and phase D in peridotitic

layers (43). While descending, slab temperatures increase and hydrous phases progressively dehydrate due to their low thermal stability (4, 5, 8, 9). The water released by the decomposition of the peridotitic hydrous minerals ascends as hydrous melts due to their low density (44) and enters the overlying basaltic layers. Here water in the hydrous melt reacts with preexisting stishovite to form hydrous aluminous poststishovite due to the high bulk Al₂O₃ content of subducted basaltic crust and the positive correlation between temperature and Al + H content. In this way, part of the water released by the destabilization of hydrous phases is actually retained within the slab in the crystal structure of poststishovite, enhancing the water storage capacity of subducted basaltic crust. While the slab keeps descending and its temperature further increases, water will not be released from the hydrous aluminous poststishovite due to the positive temperature dependence of its water solubility, allowing for H to be recycled into deeper parts of the lower mantle. Basaltic fragments containing poststishovite may work as a major water reservoir in the lower



Fig. 2. Representative polarized FT-IR spectra of poststishovite with different compositions: (A) (Si_{0.92}Al_{0.08})O₂H_{0.06} (S7546). (B) (Si_{0.90}Al_{0.11})O₂H_{0.07} (H5256).



Fig. 3. Water solubility with Al content in stishovite and poststishovite at 20 to 28 GPa and 1,200 to 1,900 °C. (A) Water contents in stishovite (St) and poststishovite (pSt) with increasing alumina content (wt %). The blue and red curves are linear fittings for St and pSt data, respectively. (B) Hydrogen incorporation into St and pSt as a function of Al content. The red line is a linear fitting for pSt data.

mantle because no other minerals can contain water under lowermantle geotherms (11–13) (Fig. 4).

An open question is how high pressure destabilizes hydrous aluminous poststishovite. In the pure SiO2 system, poststishovite transforms to seifertite at around 120 GPa, corresponding to 2,600 km depth (45), close to the core-mantle boundary (CMB). If seifertite contained only limited amounts of the AlOOH component, the AlOOH component could expand the poststishovite stability field to the higher pressures, possibly to the CMB. If it contained significant amounts, the transition pressure could shift to lower pressures. In both cases, water is transported in deeper regions than the pure poststishovite-seifertite transition (2,600 km depth). The water transported to the deep lower mantle by the silica phases may be back-transported to shallower regions by hot upwelling plumes. Geochemical studies actually suggested that ocean-island basalts produced by upwelling plumes are richer in water and contain recycled crustal materials in the source (10). Near the 660-km discontinuity, the upwelling plume may release water by the back-transformation from poststishovite to stishovite due to the weaker Al³⁺-H⁺ coupling at these pressures (Fig. 3), forming the low-velocity

layer (46) and plume ponding (47) below the 660-km discontinuity and hydrating the transition zone.

Seismic Scatterers in the Midmantle

As mentioned, seismological studies reported midmantle scatterers at 700 to 1,900 km depths, corresponding to pressures of 30 to 80 GPa, which were often interpreted by the stishovite-poststishovite transition in basalts. Although this transition occurs at much higher pressure of 55 GPa in the pure SiO₂ system (48), the current study demonstrated that the poststishovite transition can occur even at the bottom of the upper mantle by adding the AlOOH component. While the poststishovite transition is, by definition, driven by changes in pressure and temperature, we can still use the c/a and c/b determined in this study at ambient conditions (SI Appendix, Fig. S6) to infer for what Al and H contents the poststishovite transformation would take place at ambient conditions. The critical composition resulted to be 6.5 (5) mol % for poststishovite samples having Al/H ~1.5 (Fig. 3). Note that a sample with similar Al content but higher Al/H ratio transformed upon compression to about 16 GPa (24). Therefore,



Fig. 4. Water recycling in the deep mantle. Water is transported in subducting slabs down to uppermost lower mantle conditions mainly by dense hydrous phases. At depths greater than ~700 km, the water carrier becomes hydrous aluminous poststishovite (Hy-pSt). Hy-pSt will accommodate the water released from δ -AlOOH (δ), phase D and phase H (yellow). The hydrous aluminous silica phases transport water into the lowermost mantle. Upwelling hot plumes will transport water as aluminous pSt and release water (orange) around 700-km depth due to the back-transformation to stishovite (St) and its relatively low water solubility.

AlOOH-rich samples transform to poststishovite at lower pressures. If the effect of the AlOOH component on the transition pressure of stishovite is assumed to be linear, we can use the transition pressure of SiO₂ and our data (SI Appendix, Fig. S6) to determine a reduction of ~8.5 GPa/mol % AlOOH at room temperature. At high temperature, the transition pressure of stishovite increases due to its positive Clapeyron slope, which was proposed to be 65 to 88 K/GPa in pure SiO2 based on in situ X-ray diffraction measurements (49, 50). Using an average value of 76 K/GPa, we would expect silica with 5, 6, and 7 mol % AlOOH component to undergo a transformation to poststishovite at about 25 GPa and 1,200, 1,800, and 2,400 K, respectively (SI Appendix, Fig. S9). This temperature range covers the geotherms of the cold subducting slab to hot upwelling plumes. Thus, the negative shear wave velocity anomalies observed in seismic scatterers in the shallow lower mantle could be interpreted by the poststishovite phase transition in hydrous aluminous silica.

Conclusions

We have investigated phase relations in SiO_2 -Al₂O₃-H₂O system under topmost lower mantle conditions (24 to 28 GPa and 1,000 to 2,000 °C) and water solubility of aluminous stishovite and aluminous poststishovite by means of multianvil high-pressure experiment in combination with measurement of water in recovered samples by FT-IR spectroscopy. Our findings are as follows.

- Alumina contents in stishovite and poststishovite increase with increasing temperature. Aluminous stishovite was recovered when the alumina content is less than 5%, whereas CaCl₂-type aluminous silica was found to be quenchable for higher Al concentrations.
- 2) Aluminous poststishovite contains a large amount of water of weight percent levels (0.85 to 1.1 wt %). The water solubility increases with increasing alumina content.
- Hydrogen incorporation mechanism in aluminous poststishovite in the lower mantle is mainly Al³⁺-H⁺ charge coupling, and therefore, water solubility is expected to increase with temperature due to the increase of alumina content.

Our findings suggest that hydrous aluminous poststishovite is stable in a wide range of pressure-temperature conditions that are compatible with those of the ambient lower mantle and even of upwelling plumes and should thus play important roles as water reservoir and carrier in the lower mantle. The transition of stishovite to poststishovite is expected to occur at top lower-mantle conditions for 5 to 7 mol % AlOOH content and would explain the seismic scattering anomalies previously observed in this depth interval.

Materials and Methods

Starting Materials. Reagent-grade mixtures were prepared of SiO₂ (quartz) and α -AlOOH (boemite) with AlOOH fractions of 0.04, 0.05, 0.07, 0.10, 0.15, 0.20, and 0.30, and of SiO₂ and Al(OH)₃ (gibbsite) with Al(OH)₃ fractions of 0.10 and 0.15. The mixtures were ground for 1 h in an agate mortar. The SiO₂ reagent was heated at 1,000 °C for 12 h, and AlOOH and Al(OH)₃ were dried at 150 °C for 12 h prior to mixing. A reagent-grade mixture of SiO₂, Al(OH)₃, and α -FeOOH with a molar ratio of 80:15:5 was also prepared. The α -FeOOH reagent was dried at 100 °C for 12 h prior to mixing.

High Pressure-Temperature Experiments. High-pressure experiments were conducted at pressures of 24 and 28 GPa and temperatures of 1,000 to 2,000 °C for 3 to 24 h using Kawai-type multianvil presses installed at the Bayer-isches Geoinstitut, University of Bayreuth. We used 10- and 12-MN presses for

the 24-GPa experiments. The pressure calibrations are reported in ref. 51. Experiments at 28 GPa were performed using a 15-MN press with an Osugi-type guide block, IRIS-15 (52, 53). Generated pressures were reported in ref. 54. The cell assembly, which is the same as ref. 55, and the sample chambers are shown in SI Appendix, Fig. S1. A 7-mm Cr-doped MgO pressure medium was compressed using carbide anvils with 3-mm truncated edge lengths. The experimental setup of the sample chambers is shown in SI Appendix, Fig. S1. A cylindrical LaCrO₃ sleeve was adopted as the heating material. LaCrO₃ lids were placed at both ends of the heater. A powdered sample was packed in a platinum capsule and sealed by welding to avoid water leakage out of the capsule. The sample capsule was electrically insulated from the heater using an MgO sleeve and two lids. The sample temperature was monitored at the surface of the capsule using a W97%Re3%-W75%Re25% thermocouple. The ceramic components of the cell assembly were heated at 1,000 °C for more than 3 h immediately prior to assembly. The cell assembly was first compressed to the desired press load at room temperature and then heated to the target temperature at a rate of 100 °C/min. The target conditions were maintained for a desired duration, with temperature fluctuations never exceeding ± 10 °C. The temperature was then immediately reduced to room temperature by shutting off the electric power supply to the heater, and the cell assembly was slowly decompressed to ambient pressure over more than 12 to 15 h.

Analysis of Run Products. The phases present in the recovered products were identified using a microfocused X-ray diffractometer equipped with a microfocus source (IµS) of CoK α (Bruker, D8 Discover) with a two-dimensional solid-state detector (VÅNTEC-500). Several single crystals were selected from the capsules and examined using X-ray diffractometers with a CCD area detector (Oxford Diffraction, Xcalibur2) and point detector (Huber, SMC9000) operating with Mo-Ka radiation (40 to 50 kV and 30 to 40 mA). Selected crystals were orientated parallel to the (100) and (010) crystallographic planes using a Huber diffractometer for polarized FT-IR spectroscopy and then double-side polished to 14 to 199 μ m in thickness. Polarized FT-IR spectroscopy was conducted using a Bruker IFS 120 high-resolution spectrometer coupled with a Bruker IR microscope. Polarized FT-IR spectra were collected along the direction of optical extinction of each crystal platelet, which corresponded to the crystallographic directions [100] and [001] or [010] and [001] in platelets oriented parallel to the (010) and (100) planes, respectively. Unpolarized FT-IR spectra were also collected using several randomly oriented crystals. We note that water contents determined by averaging unpolarized measurements had large SDs (SI Appendix, Table S3). Rather than constituting evidence for inhomogeneous water distribution in the samples, the large calculated SDs are likely to reflect the highly anisotropic infrared absorbance of aluminous stishovite and poststishovite, which is highest perpendicular to the [001] direction and almost null parallel to the [001] direction (Fig. 2). A baseline correction was applied by subtracting from each raw spectrum using a spline function that was fitted outside the OH bands wave number region. The water contents in aluminous stishovite and poststishovite were calculated based on the method of ref. 56:

$$C_{\rm H_20} = \frac{X_i}{150\xi} \int \frac{K(\overline{\nu})}{(3780 - \overline{\nu})} d\overline{\nu} \,,$$
 [1]

where C_{H_20} is the water content (wt ppm); ξ is an orientation factor, which is 1/3 and 1 for unpolarized and polarized spectra, respectively; $K(\overline{\nu})$ is the absorption coefficient (cm⁻¹) for a given wave number $\overline{\nu}$; and X_i is a density factor given as $X_i = 18/2d \times 10^6$, where d is the mineral density (g/l) determined by singlecrystal X-ray diffraction and chemical composition analysis (SI Appendix, Table S3). The integration was conducted in the wave number range of 2,300 to $3,700 \text{ cm}^{-1}$. The water contents were also estimated by the method of ref. 57 (SI Appendix, Table S3), showing 10 to 20% higher values. We adopted water contents determined by the calibration of ref. 56 for discussion in the text. No change in water concentration was observed between the first (SI Appendix, Table S3) and second measurements with a 4-month interval. The chemical compositions of the crystals were measured using an electron probe microanalyzer with wavelength-dispersive spectrometers (JEOL, JXA-8200) at an accelerated voltage and probe current of 15 kV and 15 nA, respectively. Standard materials were quartz (SiO₂), synthetic corundum (Al₂O₃), and synthetic hematite (Fe₂O₃) for Si, Al, and Fe, respectively.

Data, Materials, and Software Availability. FT-IR and X-ray diffraction data have been deposited in Zenodo [https://doi.org/10.5281/zenodo.4972114 (58)]. All other study data are included in the article and/or *SI Appendix*.

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