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Yanhao Lin (✉ yhlin87@163.com)

CARNEGIE INSTITUTION WASHINGTON <https://orcid.org/0000-0003-0234-3157>

Qingyang Hu

Center for High Pressure Science and Technology Advanced Research <https://orcid.org/0000-0002-2742-3017>

Jing Yang

The University of Texas at Austin

Yue Meng

Carnegie Institute of Washington

Yukai Zhuang

Center for High Pressure Science and Technology Advanced Research

Michael Walter

Carnegie Institution of Science

Ho-Kwang Mao

Center for High Pressure Science and Technology Advanced Research

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Hydrous SiO₂ in subducted oceanic crust and water transport to the core-mantle boundary

Yanhao Lin^{1,2*}, Qingyang Hu^{1*}, Jing Yang², Yue Meng³, Yukai Zhuang¹, Michael J. Walter^{2*}, Ho-Kwang Mao^{1*}

¹Center for High Pressure Science and Technology Advanced Research, Shanghai 201203, People's Republic of China

²Earth and Planets Laboratory, Carnegie Institution for Science, Washington, DC 20015

³HPCAT, X-ray Science Division, Argonne National lab, Lemont, IL 60439

Subduction of oceanic lithosphere transports surface water into the mantle where it can have remarkable effects, but how much can be cycled down into the deep mantle, and potentially to the core, remains ambiguous. Recent studies show that dense SiO₂ in the form of stishovite, a major phase in subducted oceanic crust at depths greater than ~300 km, has the potential to host and carry water into the lower mantle. We investigate the hydration of stishovite and its higher-pressure polymorphs, CaCl₂-type SiO₂ and seifertite, in experiments at pressures of 44–152 GPa and temperatures of ~1380–3300 K. We quantify the water storage capacity of these dense SiO₂ phases at high pressure and find that water stabilizes CaCl₂-type SiO₂ to pressures beyond the base of the mantle. We parametrize the P-T dependence of water capacity and model H₂O storage in SiO₂ along a lower mantle geotherm. Dehydration of slab mantle in cooler slabs in the transition zone can release fluids that hydrate stishovite in oceanic crust. Hydrous SiO₂ phases are stable along a geotherm and progressively dehydrate with depth, potentially causing partial melting or silica enrichment in the lower mantle. Oceanic crust can transport ~0.2 wt% water to the core-mantle boundary region where, upon heating, it can initiate partial melting and react with the core to produce iron hydrides, providing plausible explanations for ultra-low velocity regions at the base of the mantle.

Subduction of oceanic lithosphere drives material circulation in Earth's mantle, and provides an important conduit for the deep-water cycle and the co-evolution of the hydrosphere and solid Earth. When added to mantle rocks water can significantly affect their chemical and physical properties, including mineral phase relations¹, melting temperatures^{2,3}, electrical conductivity⁴ and seismic velocities⁵ and is implicated in deep-focus earthquakes⁶. Subducted lithosphere sinks gravitationally to the base of the mantle, with the oceanic crust especially providing negative buoyancy when it becomes more dense than lower mantle rocks at depths greater than ~700 km⁷. Silica (SiO₂), as a free mineral phase, crystallizes as a major component of subducted oceanic crust (~20 wt%) at depths greater than about 300 km and undergoes several polymorphic phase changes as the crust subducts to the core-mantle boundary (CMB)^{8,9}. Stishovite, a dense SiO₂ polymorph, is stable in oceanic crust from about 300 to 1500 km, depending on temperature, where it converts to a distorted orthorhombic CaCl₂-structure^{10,11} through a second-order displacive phase transition. The CaCl₂-type phase subsequently converts to seifertite with an α PbO₂-structure near the base of the mantle at anhydrous conditions¹².

Recent work has shown that stishovite, a nominally anhydrous mineral, may host a significant amount of water in its crystal structure^{13,14}, but the water solubility in stishovite and post-stishovite SiO₂ phases remains uncertain. Here, we combine *in-situ* laser heating and high-pressure x-ray diffraction measurements to constrain the phase relations and water storage capacities (i.e., water content at saturation with a hydrous fluid or melt) of stishovite, CaCl₂-type silica and seifertite at 44–152 GPa and ~1380–3300 K. We prepared starting materials comprised of SiO₂ with four different water contents (0.5, 1.2, 3.5 and 15.2 wt%) for high-pressure experiments. Samples were heated using a double-sided laser system and held at each target temperature for ~10–15 minutes, and equations of state of Pt or Au were used as *in situ* pressure standards¹⁵. X-ray diffraction (XRD) patterns were acquired at each pressure and temperature condition and also after quenching to ambient temperature (Extended Data Fig. 1, for examples). Details of the starting compositions and experiments are described in the Methods section.

Unit cell parameters of SiO₂ phases obtained from diffraction patterns are summarized in Table 1, and are compared to volumes calculated from the equation of states (EoS) of dry silica phases^{11,12,16,17} in Fig. 1a. At quenched ambient temperature, the volumes of stishovite, CaCl₂-type SiO₂ and seifertite in our experiments are generally ~0.8–6.9%, ~1.2–5.1% and ~1.1–1.7% greater than those at the anhydrous condition at the same pressures^{12,16}, respectively. Figure 1 (b-d) shows the *in-situ* volumes of SiO₂ at high-temperature in this study relative to the thermal EoS of stishovite from Fisher *et al.*¹¹, and from the EoS from Sun *et al.*¹² for CaCl₂-SiO₂ and seifertite. The apparent negative thermal expansion in our experiments at constant pressure indicates lowering of the water storage capacity in SiO₂ with temperature, as has been observed for other nominally anhydrous phases and is explored more fully below¹⁸.

Figure 1. Measured unit cell volumes of hydrous high-pressure silica phases up to 152 GPa and 3300 K. (a) The solid and open symbols indicate silica volumes at water-saturated and water-unsaturated, respectively, and are compared with the equations of state for anhydrous stishovite from Andraut *et al.*¹⁶, CaCl₂-type silica and seifertite from Sun *et al.*¹², Fischer *et al.*¹¹ and Grocholski *et al.*¹⁷ (b-d) *In situ* high temperature volumes of stishovite (b), CaCl₂-type SiO₂ (c) and seifertite (d) compared with the thermal equations of states dry silica phases (solid curves, the literature data from Andraut *et al.*¹⁶ and Sun *et al.*¹²). Temperature uncertainties are generally less than 100 K below 2000 K and are up to 150 K at the highest temperatures.

We establish the water storage capacity in stishovite in the SiO₂-water system by observing the relationship between unit cell volume and water content in the starting composition (Fig. 2a). In principle, once a phase reaches its water saturation at constant pressure and temperature, its unit cell volume will reach a maximum and then remain constant as bulk system water content increases. We observe a linear correlation between the volume change of stishovite and the starting water contents in experiments performed at $\sim 50 \pm 6$ GPa and $\sim 1800 \pm 70$ K (Fig. 2a), as given by:

$$(V - V_{dry}) / V_{dry} = 1.86 \times C \quad (1)$$

where V is the volume of hydrous stishovite, V_{dry} is the volume of anhydrous stishovite at the same pressure and C is an initial water content in the starting composition. We find a maximum relative volume change of $\sim 6.5\%$ at ~ 3.5 wt% water in the starting composition, which we interpret as the storage capacity of stishovite at ~ 50 GPa and ~ 1800 K in the SiO₂-water system (Fig. 2a). Volume expansion was previously used to calibrate hydrous stishovite water contents at 1 bar¹⁹ but extrapolation to higher pressure is unreliable; for example, application of the calibration in combination with the EoS of hydrous stishovite to our experiment synthesized at 53 GPa (C₁₈₈) yields ~ 13 wt% water in stishovite, which is three times the water content in the starting material. However, we note the very similar

water capacity we observe for stishovite using our method and that reported previously at 9 GPa and 450 °C by Nisr *et al.*¹⁹ (~3.2 wt%).

How hydrogen is incorporated into stishovite is unknown from diffraction measurements. Possible mechanisms include cation substitution via $4\text{H}^+ \rightarrow \text{Si}^{4+}$, where hydrogen bonds to oxygen (OH^-) surrounding a Si vacancy^{14,19,20}. Other potential mechanisms include formation of a hydride (SiH_4) and incorporation of H_2O , either through an inter-crystalline substitution ($2\text{H}^+ + \text{O}^{2-} \rightarrow 2\text{O}^{2-} + \text{Si}^{4+}$) or as interstitial molecular H_2O in the stishovite lattice ($\text{SiO}_2 \cdot x\text{H}_2\text{O}$), and multiple mechanisms may occur simultaneously. Of these, interstitial H_2O may lead to the largest volume expansion, so as a first-order test of this mechanism we estimate the water content in stishovite using the equation of state of solid ice VII (ref. ²¹). This is done by adding together the volume of anhydrous stishovite at a given pressure and the ice VII volume at the same pressure (at room temperature). Remarkably, there is a nearly one-to-one correlation between the predicted water content using ice VII and that based on our starting compositions (Fig. 2a inset). This consistency strongly suggests that the large volume changes we observe result primarily by incorporation of molecular H_2O into interstitial sites (the value x listed in Table 1).

Figure 2. (a) Water contents in the bulk starting compositions versus measured unit cell volumes of hydrous stishovite relative to anhydrous stishovite ($\Delta V/V$). Red symbols are experiments at $\sim 50 \pm 6$ GPa, 1800 ± 70 K and blue symbols are experiments at other pressures and temperatures. The inset shows the water contents in the bulk starting compositions versus the water contents of hydrous stishovite calculated using the Ice VII method described in the text. (b) Pressure-temperature plot showing all experiments with 3.5 and 15.2 wt% water in the starting compositions (water-saturated). The symbols are colored according to the calculated water contents in the SiO_2 polymorph according to the scale bar.

We conducted experiments using a starting composition with 15.2 wt% H_2O at 48–102 GPa and ~ 1380 –2200 K (C_283), and 97–152 GPa and ~ 2330 –3300 K (C_154R), which we assume are all water-saturated. Estimated water storage capacities based on our Ice VII calibration are provided in Table 1 and plotted in Figure 2b, which shows an overall decrease in water capacity with increasing pressure and temperature. We fitted the calculated water capacity of stishovite and CaCl_2 -type SiO_2 to a single regression assuming all experiments made using starting compositions with 3.5 wt% and 15.2 wt% H_2O were

water-saturated and with pressure and temperature as independent variables, yielding the equation:

$$\text{H}_2\text{O (wt\%)} = 4.1 (9) - 0.042 (7) P (\text{GPa}) + 45 (31) 1/T (\text{K}) \quad (R^2 = 0.85) \quad (2)$$

Overall our limited dataset is well reproduced by this expression as indicated by the goodness of fit (Extended Data Fig. 2), although we note that the $1/T$ term has considerable uncertainty. As expected from Fig. 2b, the regression predicts that water capacity decreases with both pressure and temperature. Figure 3 shows the predicted water capacity of SiO_2 phases along a mantle geotherm on the basis of our regression. At upper mantle pressures where stishovite first appears in oceanic crust it can hold ~ 3.5 wt% water even at mantle temperatures. The P-T dependence continually reduces the water capacity to less than 1 wt% at the CMB, as discussed below.

Figure 3. Modelled water capacity (blue curve) of stishovite and CaCl_2 -type SiO_2 as a function of pressure along an idealized mantle geotherm (red curve²²). The water capacity decreases continuously from >3.5 wt% H_2O in the transition zone to < 1 wt% near the core mantle boundary.

The phase transition boundaries under water-saturated conditions were bracketed between stishovite and CaCl_2 -type SiO_2 at 75 ± 3 GPa and ~ 1860 K (C_283), and between CaCl_2 -type SiO_2 and PbO_2 -type SiO_2 (seifertite) at 138 ± 4 GPa and ~ 2700 – 2850 K (C_154R) (Fig. 2b). The transition boundary between stishovite and CaCl_2 -type SiO_2 is not significantly shifted from the dry silica system (e.g. ~ 74 GPa and ~ 1900 K summarized in Fischer *et al.*¹¹), which is consistent with an indistinguishable high water storage capacity predicted for stishovite and the CaCl_2 -type polymorph; for example, the calculated water content of stishovite at 65.5 GPa and 1804 K and in CaCl_2 -type silica at 82.5 GPa and 1810 K is ~ 3 wt% for both. We estimate the transition to seifertite at a pressure of ~ 140 GPa at ~ 3000 K, or ~ 20 GPa higher than in the dry system¹², consistent with a lower water content for seifertite (< 1 wt%) relative to CaCl_2 -type SiO_2 .

165 In experiments where seifertite crystallized ($> \sim 140$ GPa) using the bulk composition with
166 15.2 wt% water, we observe a new coexisting solid phase that is well indexed to silicon
167 hydride, SiH_4 (Extended Data Fig. 1c). The presence of this phase, even at temperatures in
168 excess of 3000 K, indicates that hydrides could be important in the interiors of large, wet,
169 rocky exoplanets, and their crystallization can also be a source of oxygen. These results
170 need to be explored more fully and are not the focus here, but we note that the stability of
171 SiH_4 can potentially provide a source of hydrogen in Earth's core.

172
173 Free silica phases are unexpected in most or all of Earth's mantle because the Mg/Si ratio
174 of primitive upper mantle peridotite is greater than unity (~ 1.1)²³. Modeling of seismic
175 velocity observations are permissive of a lower mantle composition with a Mg/Si ratio
176 nearer unity^{24,25}, but even these compositions are not expected to contain a free silica phase.
177 In contrast, oceanic crust has a low Mg/Si ratio much less than unity and, therefore, free
178 silica phases have the potential to host and transport water into the deep mantle in
179 subducted slabs. However, this does not mean that water is available for transport.

180
181 Water is added to the oceanic crust through hydrothermal alteration at the mid-ocean ridge
182 and hydration at the surface of the slab. Plate-bending at the outer rise results in fracture
183 development in the deforming plate, with fractures penetrating through the crust and
184 extending some 20–30 km into the slab mantle, allowing seawater to circulate deeply to
185 serpentinize mantle lithosphere^{26–29}. Dehydration of oceanic crust is very efficient beneath
186 the volcanic front and is expected to be nearly complete at depths < 250 km^{30,31}, shallower
187 than the depths where stishovite first crystallizes (~ 300 km). Likewise, in hotter subduction
188 zones serpentine in the slab mantle is also expected to extensively dehydrate at depths $<$
189 ~ 250 km due to a depression in the dehydration phase boundaries at ~ 6 GPa (Extended
190 Data Fig. 3). However, in cooler subduction zones dehydration can be avoided, and water
191 can be transported into the transition zone hosted in post-serpentine hydrous phases (e.g.
192 phase E, superhydrous phase B, and phase D)^{31,32}. Estimates based on phase relations and
193 slab thermal profiles suggest that in cooler slabs ~ 4 – 5 wt% water can be stored in hydrated
194 portions of mantle lithosphere^{33,34}.

195
196 Silica phases provide a mechanism to transport water released from the slab in the
197 transition zone into the lower mantle and all the way to the CMB. As slabs stagnate and
198 heat up in the transition zone due to buoyancy and rheological effects accompanying phase
199 changes^{35,36}, water may be released through dehydration of post-serpentine phases^{33,37}
200 (Extended Data Fig. 3). Even without stagnation, phase relations indicate that by ~ 1000
201 km any water held in slab lithosphere will be released when superhydrous phase B or Phase
202 D breaks down to form bridgmanite ($\pm$ periclase or stishovite) coexisting with a hydrous
203 fluid or melt phase. Percolation of water-rich fluids into the adjacent oceanic crust, possibly
204 along pre-existing fracture systems related to lithospheric hydration, creates the
205 opportunity for hydration of stishovite. At transition zone pressures and temperatures
206 stishovite can accommodate ~ 3.5 wt% water (~ 0.7 wt% in bulk crust) and, depending on
207 the efficiency of the fluid migration process, oceanic crust can potentially accommodate
208 all of the released water.

A simple estimate of the capacity of subducted oceanic crust to hydrate the deep mantle, on the basis of silica phases in oceanic crust alone, can be made for modern Earth using an average subduction rate (5 cm yr^{-1}), global length of subduction zones (46,000 km) and mean crustal thickness (6 km) (ref. ³⁸), and assuming a conservative water capacity of hydrous stishovite in oceanic crust of 3 wt% in the transition zone. This calculation yields $\sim 1.4 \times 10^{21} \text{ kg}$ water, or about one ocean mass, over 4 billion years of subduction. While a more precise accounting requires knowledge of the water storage capacity of all coexisting phases, given that current estimates of total mantle water content are about one ocean mass on the basis of geochemical arguments³⁹, and that modeling of water transport into the deep mantle by subduction over Earth's history yields a similar value³¹, we find that SiO_2 phases provide a quantitatively plausible explanation for hydrating the deep mantle. If the mantle currently has about one ocean mass of water³⁹ that has been obtained through plate tectonic recycling, the implication is that the initial mantle was nearly anhydrous, perhaps owing to higher mantle temperatures in the early Earth⁴⁰ resulting in near-complete early mantle dehydration; this is also consistent with isotopic data indicating more than one ocean of water at the Earth's surface in the Archean^{41,42}.

Direct evidence for slab water release in the transition zone and uppermost lower mantle comes from inclusions in sublithospheric diamonds. Although exceedingly rare, the presence of a hydrous ringwoodite inclusion in a diamond suite from Brazil, whose provenance has been related to subducted lithosphere, provides direct evidence for local hydration⁴³. Further, boron-, oxygen, carbon and nitrogen isotopes of diamonds and their inclusions derived from the base of the transition zone and uppermost lower mantle indicate a direct role for aqueous fluids associated with seawater serpentinization near the surface and eventual dehydration of slab lithosphere at the base of the transition zone^{44,45}.

A link between dehydration of slab mantle in cooler subducting slabs in the transition zone and deep focus earthquakes has been postulated⁴⁶, and given its propensity for hydration, stishovite could play a role in whichever of the competing mechanism leads to deep seismicity⁴⁷. The process depicted in Fig. 4, where stishovite in oceanic crust is hydrated by the release of mantle fluids along pre-existing slab faults and cracks, is accompanied by a substantial positive volume change. For example, fully hydrating stishovite in oceanic crust at 20 GPa results in an $\sim 6.5\%$ volume increase, which, when ignoring partitioning with other anhydrous minerals, results in an $\sim 1.3\%$ volume increase in the whole rock. This very large, positive volume change would create $\sim 5 \text{ GPa}$ overpressure above the hydrostatic load at 20 GPa, locally creating high compressive stresses. The role that stishovite hydration and expansion might play in deep focus earthquake mechanisms requires further investigation.

Hydration of stishovite in the transition zone provides a conduit for water to the deep lower mantle and core. We note that other hydrous phases can also crystallize in oceanic crust at high pressures, including Phase D, Phase H and $\delta\text{-AlOOH}$ (ref. ¹⁸), but these phases would only stabilize after saturation of primary silica phases with water and other coexisting nominally anhydrous phases in oceanic crust (Extended Data Fig. 4). Perhaps more importantly, these phases have a much lower temperature stability^{18,48}. Figure 3 shows that stishovite will enter the lower mantle with $>3 \text{ wt\%}$ water even along a mantle geotherm,

but will progressively dehydrate (as CaCl_2 -type SiO_2 at >75 GPa) as it transits the mantle to the core mantle boundary region. Hydrous fluids or melts released in this way may percolate away from the slab into the ambient mantle resulting in crystallization of aluminous Phase H (Extended Data Fig. 4), but at temperatures of the mantle geotherm a hydrous partial melt is predicted on the basis of experimental phase relations⁴⁸. While we have no compositional information about these fluids, it is likely that they will be supercritical solutions at these high pressures and temperatures such that they could enrich the lower mantle locally in a dissolved silica component, converting ferropericlase to bridgmanite, and possibly stabilizing a free, and hydrated, silica phase that is stable at mantle temperatures.

Upon arrival just above the CMB (~ 120 GPa) CaCl_2 -type SiO_2 may carry about 0.8 wt% water (~ 0.2 wt% in bulk crust), but the superadiabatic temperature gradient above the core mantle boundary⁴⁹ would induce nearly complete dehydration ($< 0.04\%$ in bulk crust) as crust sinks to the CMB (Fig. 4). Release of water in this region may generate partial melting due to the effect of water on lowering the solidus of peridotite by hundreds of degrees⁵⁰ and changing the mineral assemblage⁵¹. Reaction of released water with the iron-metal outer core may also crystallize new high-pressure phases (e.g., FeO_2H_x , FeH_5)^{52–56}. Production of partial melt and iron hydride phases have both been shown to provide plausible explanations for the observed seismic anisotropy⁵⁷ and anomalously slow P-wave velocities⁵⁸ at the base of Earth's mantle (Fig. 4). Water-bearing fluids released at the core-mantle boundary could also hydrate SiO_2 expelled from the core and accumulated at the CMB before buoyant diapiric upwelling⁵⁹. Similarly, water expelled from the slab in the lower mantle may be incorporated into silica diapirs as they rise from the CMB to the mid- or upper-lower mantle. Hydration of silica phases in subducted oceanic crust and their unparalleled capacity to host significant amounts of water even at high mantle temperatures provides a unique mechanism for transport and storage of water to the deepest mantle.

Figure 4. A schematic model for transport of water into the deep mantle in hydrous silica phases. Water is added to slab crust and mantle near the surface through interaction of seawater with the crust and through faults and cracks in the lithosphere formed by slab bending at the outer rise. Oceanic crust extensively dehydrates at <200 km depth, but slab mantle can carry water into the transition zone in hydrous phases in cooler slabs. Dehydration of hydrous phases in slab mantle in the transition zone generates hydrous fluids that migrate along fractures to the oceanic crust where they hydrate stishovite (~3.5 wt% water). Stishovite transports water into the lower mantle where it converts to CaCl₂-type SiO₂, and the water capacity of these phases decreases continuously as the slab transits the lower mantle, potentially releasing hydrous fluids to the mantle that may cause melting and potentially enrich the mantle in silica. The rapid increase in temperature near the core-mantle boundary may release a pulse of water that can induce partial melting⁵⁰ and/or the crystallization of iron-hydride phases (e.g., FeO₂H_x, FeH₅)⁵²⁻⁵⁶ upon reaction with the metallic iron core, potentially leading to regions of ultra-low seismic velocity. Fluid release may also hydrate silica-rich domains at the core-mantle boundary formed through exsolution from the core.

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441 **Table 1. Summary of experimental results.**

Exp.	Water at starting comp. (wt.%)	T (K)		<i>a</i> (Å)	<i>b</i> (Å)	<i>c</i> (Å)	<i>V</i> (Å ³) / f.u.	1 Sigma (Å ²)	P (GPa) / Pt or Au	<i>V</i> (dry) (Å ³)	ΔV (Å ³) (=V _{wet} -V _{dry})	$\Delta V/V$ (%)	<i>V</i> (Ice VII) (Å ³)	<i>x</i> (H ₂ O)	<i>C</i> * (H ₂ O, wt.%)	
		T_LH (K)	T_XRD (K)													
S_241 [97 mol.% SiO ₂ + 3 mol.% Silic acid + Pt black]																
Stishovite																
Run1_1	0.5	1850	300	4.015	4.015	2.594	20.831	0.015	44.0	20.667	0.164	0.79	11.998	0.01	0.41	
S_242 [93 mol.% SiO ₂ + 7 mol.% Silic acid + Pt black]																
Stishovite																
Run1_1	1.2	1850	300	4.020	4.020	2.602	21.020	0.018	48.0	20.667	0.353	1.71	11.736	0.03	0.89	
C_188 [75 mol.% SiO ₂ + 25 mol.% Silic acid + Pt black]																
Stishovite																
Run1_5	3.5	1401	300	4.078	4.078	2.629	21.864	0.014	53.0	20.468	1.395	6.82	11.431	0.12	3.53	
Run2_3		1382	300	4.076	4.076	2.628	21.835	0.024	54.0	20.430	1.404	6.87	11.373	0.12	3.57	
Run2_5		1537	300	4.072	4.072	2.628	21.787	0.022	54.5	20.412	1.375	6.74	11.344	0.12	3.51	
Run2_11		1857	300	4.065	4.065	2.625	21.691	0.013	56.0	20.337	1.354	6.66	11.260	0.12	3.48	
C_283 [Silic acid + Au]																
Stishovite																
Run1_1	15.2	1382	300	4.084	4.084	2.635	21.974	0.019	48.0	20.667	1.307	6.32	11.74	0.11	3.23	
Run1_2		1727	300	4.075	4.075	2.629	21.826	0.018	50.5	20.569	1.258	6.12	11.58	0.11	3.16	
Run2_1		1651	300	4.025	4.025	2.602	21.077	0.021	67.5	19.956	1.121	5.62	10.18	0.11	3.20	
Run2_2		1865	300	4.009	4.009	2.599	20.885	0.021	72.5	19.793	1.092	5.52	10.01	0.11	3.17	
Run2_3		1804	300	4.022	4.022	2.604	21.059	0.018	65.5	19.990	1.070	5.35	10.76	0.10	2.89	
CaCl ₂ -type SiO ₂																
Run3_1		1810	300	4.078	3.910	2.551	20.338	0.017	82.5	19.345	0.993	5.13	9.70	0.10	2.98	
Run3_2		1855	300	4.095	3.913	2.545	20.387	0.017	77.5	19.527	0.861	4.41	9.84	0.09	2.56	
Run4_1	15.2	1828	300	4.071	3.879	2.511	19.831	0.017	88.0	19.154	0.677	3.53	9.58	0.07	2.08	
Run5_1		2203	300	4.036	3.876	2.514	19.661	0.017	94.5	18.939	0.723	3.82	9.42	0.08	2.25	
Run6_1		2191	300	4.002	3.863	2.518	19.463	0.016	102.5	18.687	0.776	4.15	9.27	0.08	2.45	
C_154R [Silic acid + Pt black]																
CaCl ₂ -type SiO ₂																
Run1_2	15.2	2330	300	4.008	3.815	2.498	19.099	0.016	97.0	18.859	0.240	1.27	9.38	0.03	0.76	
Run3_1		2604	300	3.959	3.761	2.469	18.379	0.016	120.5	18.170	0.209	1.15	8.97	0.02	0.69	
Run4_1		2695	300	3.956	3.718	2.456	18.065	0.015	134.5	17.808	0.257	1.44	8.78	0.03	0.87	
Run4_2		2846	300	3.955	3.725	2.456	18.089	0.015	133.0	17.845	0.244	1.37	8.80	0.03	0.82	
PbO ₂ -type (Seifertite)																
Run5_1	15.2	3280	300	3.738	4.602	4.099	17.630	0.042	147.5	17.328	0.301	1.74	8.62	0.03	1.04	
Run5_2		2853	300	3.724	4.603	4.117	17.643	0.040	141.5	17.459	0.184	1.06	8.69	0.02	0.63	
Run7_1		3054	300	3.707	4.602	4.107	17.519	0.031	152.0	17.233	0.285	1.65	8.58	0.03	0.99	
Run7_2		3296	300	3.715	4.590	4.105	17.495	0.031	150.0	17.275	0.220	1.27	8.60	0.03	0.76	
T_LH, the aim temperature before temperature quenched; T_XRD, the room temperature when all XRD shown here were collected;																
T, temperature; Temperature errors are generally below 100 K at the aim temperature lower than 2000 K and are up to 150 K at the highest temperature achieved; P, pressure; the pressure is shown by the Pt or Au calibration ¹⁵ ;																
<i>V</i> (dry) is calculated at the relative pressure and room temperature from Andraut <i>et al.</i> ¹⁶ for stishovite and Sun <i>et al.</i> ¹² for CaCl ₂ -type and PbO ₂ -type silica phases;																
<i>C</i> *, water concentration is calculated based on a proportional relation between the volume of ice VII (ref. 21) and the volume change (ΔV) at the same pressures; <i>x</i> represents water content in SiO ₂ · <i>x</i> H ₂ O.																

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Methods

Starting materials and experimental design. The starting compositions were mixtures of amorphous SiO₂ (1 μm grain size, purity 99.999%) and silic acid (SiO₂ · 0.6H₂O, 15.2 wt% water) in different proportions (Table 1). About 10 wt% amorphous Pt or Au powder was added to the mixture for infrared laser absorption in laser heating experiment. The mixtures were ground for 4–6 hours.

The first type of starting material was only silic acid with ~15.2 wt% H₂O (the two experiments: C_283 and C_154R). In the experiment C_283, the sample was loaded in a 100 μm diameter hole in a rhenium gasket indented by diamond anvils with 200 μm diameter culet. As for C_154R, the sample was loaded in a 45 μm diameter hole in a rhenium gasket indented by diamond anvils with 90 μm diameter culet beveled from 400 μm culet. The second type of starting materials was a mixture of amorphous SiO₂ and silic acid with the different target water contents (0.5 wt% (S_241), 1.2 wt% (S_242) and 3.5 wt% (C_188)). Each sample was respectively loaded in a 120 μm diameter hole in a rhenium gasket indented by diamond anvils with 250 μm diameter culet. Except the sample C_283 with Au powder, the other four samples were mixed with Pt black. Pressures were determined before and after heating by the self-consistent equation of states (EOS) of the doped Pt or Au¹⁵, and the error bar of calibrated pressure is estimated to be of the order 1 to 2 GPa.

Samples were heated in a double-sided laser-heated diamond-anvil cell (DAC) and examined *in situ* at high pressures and temperatures by synchrotron x-ray powder diffraction at High Pressure Collaborative Access Team (HPCAT) of the Advanced Photon Source, Argonne National Laboratory⁶⁰ and at the BL15U1 beamline, Shanghai Synchrotron Radiation Facility (SSRF) in China⁶¹. The X-ray beam size was 2.9×5.4 μm² with a wavelength of 0.4066 Å at HPCAT and was 1.0×3.0 μm² with a wavelength of 0.6199 Å at SSRF. For laser heating, the diameter of a laser heating spot was up to ~30 μm at ~3300 K in the flat top area created with a focused yttrium lithium fluoride laser using a double-sided heating technique that minimizes both radial and axial temperature gradients. Temperatures were determined by fitting the thermal radiation from the central portion of the heated spot to the Planck radiation function^{60,61}.

Data availability The authors declare that all relevant data supporting this study are available within the paper or available on request from the corresponding authors.

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Author Contributions

Y.L., Q.H., M.J.W. and H.-k.M. designed the research; Y.L., J.Y., M.J.W. and Y.M. performed experiments; Q.H., Y.L., M.J.W. and H.-k.M. analyzed data; and Y.L., Q.H and M.J.W. wrote the paper with input from all authors. Y.L., Q.H., M.J.W. and H.-k.M. contributed equally to this work.

Competing interests

The authors declare no competing interests.

Additional information

Correspondence and requests for materials should be addressed to Y.L. (yhlin@carnegiescience.edu), Q.H. (qingyang.hu@hpstar.ac.cn), M.J.W. (mwalter@carnegiescience.edu) or H.-K.M. (maohk@hpstar.ac.cn).

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Extended Data Fig. 1 | Representative X-ray diffraction patterns at 68, 84 and 142 GPa (Au pressures), 300 K after laser heating. Green, blue and red ticks represent the calculated diffraction peaks for water-bearing stishovite (a), CaCl₂-type SiO₂ (b) and seifertite (c) (details in Table 1), respectively. In addition, a SiH₄ phase is confirmed as well at 142 GPa (c). Data were acquired using an X-ray wavelength of 0.4066 Å. Stv = stishovite, Ccl = CaCl₂-type SiO₂, Sft = seifertite.

Extended Data Fig. 2 | Diagram showing the regressed water content and the calculated water content in stishovite and CaCl₂-type SiO₂ in all water-saturated experiments. The line shows an ideal 1:1 correspondence.

Extended Data Fig. 3 | Pressure-temperature diagram showing phase relations for water-saturated peridotite^{32,33,37}. Phase labels designate generalized regions of stable hydrous magnesian silicates: ant=antigorite; PhA=phase A; PhE=phase E; PhD=phase D; SHB=superhydrous phase B; wad=wadsleyite; ring=ringwoodite; brg=bridgmanite. Water contents of peridotite at saturation are from Komabayashi and Omori³³. Average geotherms for cool and warm slabs are shown for peridotite at the Moho (blue and purple arrows) and for the top of the oceanic crust (orange and red arrows) and are after Van Keken *et al.*³¹. The inset is taken from Fig. 4 in the main text and shows an idealized model of dehydration in the transition zone of serpentinized mantle along fractures and percolation of fluids into adjacent crust where stishovite hydration occurs.

Extended Data Fig. 4 | Schematic compatibility diagrams in the system MgO-SiO₂-H₂O (mols). The upper diagram illustrates phase compatibility at upper lower mantle conditions (50 GPa) and the lower plot at conditions near the core-mantle boundary (120 GPa). At 50 GPa, stishovite can hold ~3 wt% water whereas at 120 GPa it holds < 1 wt% water. Hydrous phases only crystallize in model hydrated oceanic crust (blue symbol) when bulk compositions lie within the three-phase triangle, e.g. SiO₂ - Phase H - bridgmanite (Brd).

Figures

Figure 1

Measured unit cell volumes of hydrous high-pressure silica phases up to 152 GPa and 3300 K. (a) The solid and open symbols indicate silica volumes at water-saturated and water unsaturated, respectively, and are compared with the equations of state for anhydrous stishovite from Andrault et al.16, CaCl_2 -type silica and seifertite from Sun et al.12, Fischer et al.11 and Grocholski et al.17 (b-d) In situ high temperature volumes of stishovite (b), CaCl_2 -type SiO_2 (c) and seifertite (d) compared with the thermal equations of states dry silica phases (solid curves, the literature data from Andrault et al.16 and Sun et al.12). Temperature uncertainties are generally less than 100 K below 2000 K and are up to 150 K at the highest temperatures.

Figure 2

(a) Water contents in the bulk starting compositions versus measured unit cell volumes of hydrous stishovite relative to anhydrous stishovite ($\Delta V/V$). Red symbols are experiments at $\sim 50 \pm 6$ GPa, 1800 ± 70 K and blue symbols are experiments at other pressures and temperatures. The inset shows the water contents in the bulk starting compositions versus the water contents of hydrous stishovite calculated using the Ice VII method described in the text. (b) Pressure temperature plot showing all experiments with 3.5 and 15.2 wt% water in the starting compositions (water-saturated). The symbols are colored according to the calculated water contents in the SiO_2 polymorph according to the scale bar.

Figure 3

Modelled water capacity (blue curve) of stishovite and CaCl₂-type SiO₂ as a function of pressure along an idealized mantle geotherm (red curve²²). The water capacity decreases continuously from >3.5 wt% H₂O in the transition zone to < 1 wt% near the core mantle boundary.

Figure 4

A schematic model for transport of water into the deep mantle in hydrous silica phases. Water is added to slab crust and mantle near the surface through interaction of seawater with the crust and through faults and cracks in the lithosphere formed by slab bending at the outer rise. Oceanic crust extensively dehydrates at <200 km depth, but slab mantle can carry water into the transition zone in hydrous phases in cooler slabs. Dehydration of hydrous phases in slab mantle in the transition zone generates hydrous fluids that migrate along fractures to the oceanic crust where they hydrate stishovite (~3.5 wt% water). Stishovite transports water into the lower mantle where it converts to CaCl_2 -type SiO_2 , and the water capacity of these phases decreases continuously as the slab transits the lower mantle, potentially releasing hydrous fluids to the mantle that may cause melting and potentially enrich the mantle in silica. The rapid increase in temperature near the core mantle boundary may release a pulse of water that can induce partial melting⁵⁰ and/or the crystallization of iron-hydride phases (e.g., FeO_2H_x , FeH_5)^{52–56} upon reaction with the metallic iron core, potentially leading to regions of ultra-low seismic velocity. Fluid release may also hydrate silica-rich domains at the core-mantle boundary formed through exsolution from the core.