# Does water escape from subducted slabs at the core-mantle boundary?

Hydrated $SiO_2$ phase is the main carrier of water in the subducting slabs of the Earth's lower mantle. Recent experiments performed along cold-to-normal lower-mantle geotherms have demonstrated that $SiO_2$ can hold up to ~3.5 wt% $H_2O$ [1,2]. Regardless of the high water holding capacity of dense $SiO_2$, it has been speculated that subducted slabs will dehydrate at high temperatures in the core-mantle boundary (CMB) region, and the released water will give rise to chemical heterogeneities, as indicated by seismological observations. Water can induce melting, melt migration, and hydration of the lowermost mantle materials, creating large low-shear-velocity provinces. Furthermore, the reaction of water with the core metal can form superoxidized $FeOOH_x$ ($x < 1$), which accounts for ultralow velocity zones. Nevertheless, the solubility and partitioning of water into Al-bearing hydrous $SiO_2$ within subducted former crustal rocks, especially mid-oceanic ridge basalt (MORB), have not been investigated under the high pressure and temperature ($P$–$T$) conditions in the CMB region; therefore, the dehydration of subducted slabs and its associated effects remain unverified.

We conducted 19 separate melting experiments on hydrous MORB up to the lowermost mantle pressure range at 4100 K in a laser-heated diamond-anvil cell by collecting X-ray diffraction (XRD) patterns at SPring-8 **BL10XU** [3]. Melting textures and chemical compositions, including the $H_2O$ content in the melt and coexisting solids, were examined in the recovered samples. They exhibited a concentric texture: a round pocket of quenched partial melt at the center surrounded by a $SiO_2$ phase, $CaSiO_3$ perovskite (davemaoite), $SiO_2$–AlOOH solid solution (ss.) and bridgmanite at 25–59 GPa (Fig. 1(a)). At 100 GPa and above, $SiO_2$ was still present next to the melt pool, and the bridgmanite/post-perovskite appeared closer to the melt than it did at lower pressures (Fig. 1(b)). The XRD patterns of these samples indicated that $CaCl_2$-type $SiO_2$ appeared down to at least 25 GPa at 2900 K. This observation is consistent with earlier findings that $CaCl_2$-type $SiO_2$ stabilizes over stishovite in the presence of $Al_2O_3$ and $H_2O$ [2], whereas it forms above 65–75 GPa at 1500–2000 K in Al-free dry $SiO_2$ and $SiO_2$–$H_2O$ systems [1]. Furthermore, the crystal structure of $SiO_2$ transformed from $CaCl_2$-type to $\alpha$-$PbO_2$-type (seifertite) above 128 GPa in the lowermost mantle (Fig. 2).

Water concentrations in the $SiO_2$ phase, $SiO_2$–AlOOH ss., and partial melts were determined by

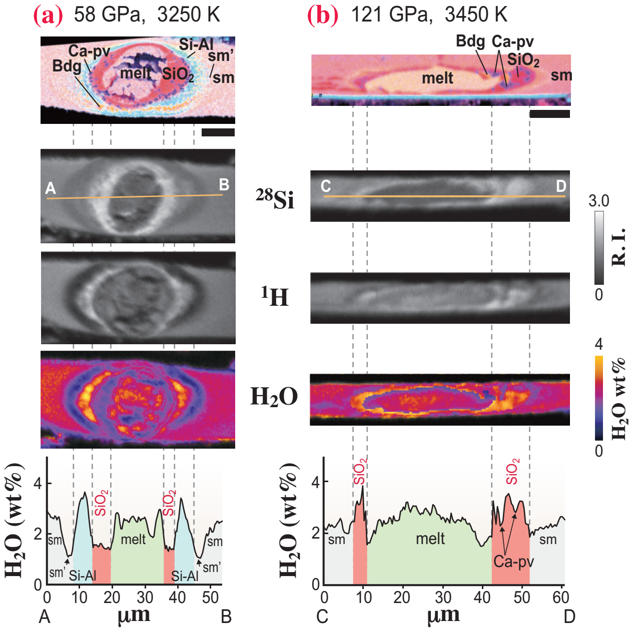

Fig. 1. Cross sections of partially molten samples. Samples were recovered from (**a**) 58 GPa and 3250 K and (**b**) 121 GPa and 3450 K. (Uppermost panels) EDS X-ray elemental maps combined for Si, Al, Ca, and Mg, showing melt, hydrated $SiO_2$ (red), $CaSiO_3$ perovskite (Ca-pv; blue), $SiO_2$–AlOOH ss. (Si–Al; light blue), bridgmanite (Bdg; orange), and dehydrated (sm') and original starting material (sm). (Middle panels) Corresponding secondary ion images for $^{28}Si^+$ and $^{1}H^+$ and the distribution maps of $H_2O$. Scale bar: 10 µm.

secondary ion mass spectrometry coupled with high-resolution imaging (Fig. 1). The water content in Al-bearing $CaCl_2$-type $SiO_2$ substantially increased with increasing pressure, reaching 3.6 wt% $H_2O$ at 121 GPa under 3450 K (Figs. 2(a,b)). This value is considerably higher than the recent $H_2O$ solubility estimate of only 0.4 wt% under the same $P$–$T$ condition based on experiments on the Al-free $SiO_2$–$H_2O$ system [1]. This discrepancy suggests that the charge-coupled substitution $Si^{4+} = Al^{3+} + H^+$ is the key mechanism for water incorporation into Al-bearing $CaCl_2$- [2] and $\alpha$-$PbO_2$-type $SiO_2$ (Fig. 2(c)). Our XRD study found that the magnitude of the orthorhombic distortion increased with increasing pressure (Fig. 2(d) and Fig. 3), and this crystallographic distortion correlated strongly with the water content (Fig. 2(e) and Fig. 3). The enhanced distortion shortened the distance between specific pairs of oxygen atoms, making the hydrogen bonds stronger and stabilizing hydrogen in $SiO_2$. Moreover, the overall increase in water concentration in $CaCl_2$-type $SiO_2$ with increasing pressure resulted in an increase in the partition coefficient of water ($D_{H_2O}$ ($CaCl_2$–$SiO_2$/melt)) from ~0.2 at 25 GPa to 1.4 under deep lower-mantle conditions at 120 GPa (Fig. 2(f)). The $H_2O$ content in Al-bearing $\alpha$-$PbO_2$-type $SiO_2$, formed at 3650–4100 K and 128–144 GPa—conditions corresponding to the Earth's CMB region—remained nearly constant at 2 wt% (Fig. 2(a)). Moreover, $D_{H_2O}$ ($\alpha$-$PbO_2$–$SiO_2$/melt) ranged from 1.1 to 2.1 (Fig. 2(f)), indicating that water preferentially partitions into hydrated $SiO_2$ rather than into coexisting partial melts under CMB conditions.

The dehydration of subducted slabs at the base of the mantle has been highlighted, and its consequences have been extensively discussed. However, our discovery of the high $H_2O$ storage capacity—approximately 2 wt% in $\alpha$-$PbO_2$-type $SiO_2$ and ~0.3–0.6 wt% in subducted MORB crust—suggests that, in practice, water does not escape from slabs even under the high temperature conditions of the CMB region.

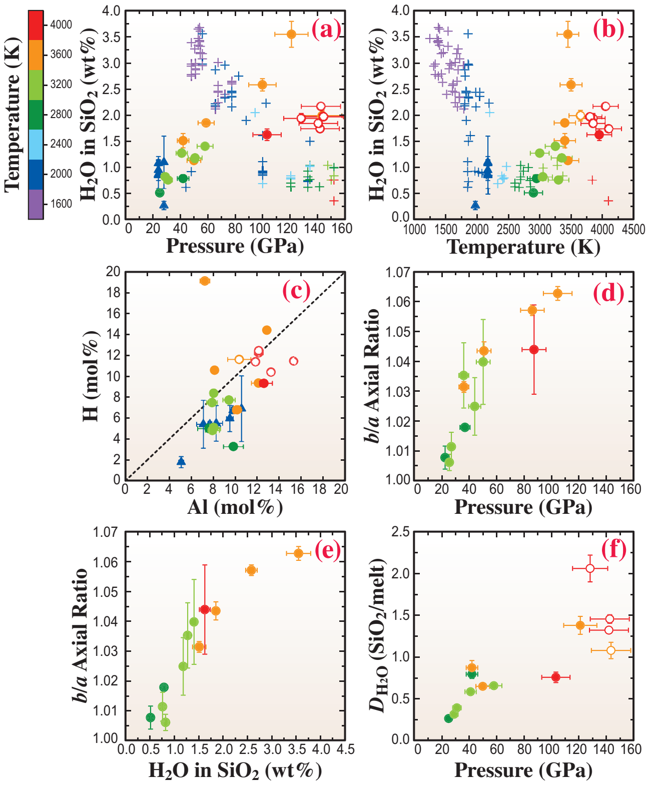

Fig. 2. Variations in hydrated $SiO_2$. The present experiments on hydrous MORB show data for $CaCl_2$-type (closed circles) and $\alpha$-$PbO_2$-type $SiO_2$ (open circles). Earlier data obtained in water-saturated $SiO_2$–$H_2O$ (pluses) [1] and $SiO_2$–$Al_2O_3$–$H_2O$ systems (triangles) [2] are also given. Color indicates temperature. Water concentrations in $SiO_2$, plotted as functions of **(a)** pressure and **(b)** temperature. **(c)** Correlation between Al and H concentrations in $SiO_2$, indicating that the charge-coupled substitution $Si^{4+} = Al^{3+} + H^+$ is a main mechanism for water incorporation. **(d)** $b/a$ axial ratio of the $CaCl_2$-type structure observed at 300 K, representing the magnitude of the orthorhombic distortion from a tetragonal structure with $b/a = 1$. **(e)** Correlation between the $H_2O$ content and $b/a$ ratio. **(f)** $SiO_2$/melt partition coefficient of $H_2O$, demonstrating that water is preferentially partitioned into $SiO_2$ rather than into silicate melt in the lowermost mantle.

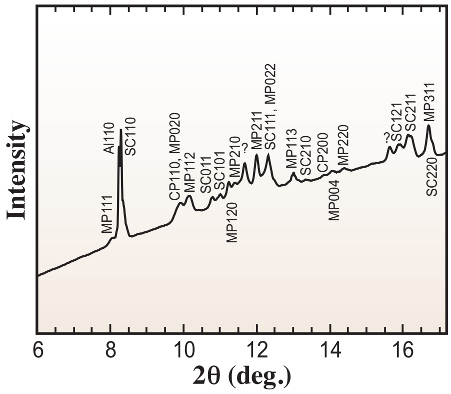

Fig. 3. XRD patterns of the solid part around a melt pocket obtained after quenching. SC, hydrated $CaCl_2$-type $SiO_2$; MP, bridgmanite; CP, $CaSiO_3$ perovskite; Al, $SiO_2$–AlOOH ss. Peak separations of SC121/211 and SC011/101 indicate the orthorhombic distortion of the $CaCl_2$-type structure.

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## References

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