

## **Water-induced Diamond Formation at Earth's Core-Mantle Boundary**

Byeongkwan Ko<sup>1\*</sup>, Stella Chariton<sup>2</sup>, Vitali Prakapenka<sup>2</sup>, Bin Chen<sup>3</sup>, Edward J. Garnero<sup>1</sup>,  
Mingming Li<sup>1</sup>, Sang-Heon Shim<sup>1</sup>

<sup>1</sup>School of Earth and Space Exploration, Arizona State University, Tempe, AZ, USA

<sup>2</sup>Center for Advanced Radiation Sources, University of Chicago, Chicago, IL, USA

<sup>3</sup>Hawaii Institute of Geophysics and Planetology, University of Hawaii at Manoa, Honolulu, HI, USA

\*Now at Department of Earth and Environmental Sciences, Michigan State University, East Lansing, MI, USA

Corresponding author: Byeongkwan Ko (kobyong@msu.edu)

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### **Introduction**

This supporting information provides the supplementary texts and figures to support the main article.

### Text S1. X-ray diffraction patterns after temperature-quench at high pressures

After temperature-quench, X-ray diffraction (XRD) patterns show many more peaks. In some patterns, diffraction lines of py-FeOOH<sub>x</sub> and fcc-FeH<sub>x</sub> remain upon the temperature-quench. However, there were many more lines and they were difficult to interpret. In some patterns, we observed  $\epsilon$ -FeOOH<sub>x</sub> instead of the pyrite-type FeOOH with additional diffraction lines which could not be interpreted. It is possible that a range of temperatures during quench process could have resulted in formation of metastable phases in Fe-O-H-C. We conjecture that the unassigned peaks may come from iron hydride phase (dhcp-FeH<sub>x</sub>, FeH<sub>2</sub>, or FeH<sub>3</sub>) and iron oxide phase ( $\eta$ -Fe<sub>2</sub>O<sub>3</sub> or Fe<sub>2</sub>O<sub>3</sub> in post-perovskite structure). However, the assignments for these metastable phases remain inconclusive.

### Test S2. Estimation of chemical exchange between the mantle and the core

The number of moles of H<sub>2</sub>O required to form a mole of C,  $NR(H_2O/C)$ , through the reaction between water and the core can be calculated from:

$$NR(H_2O/C) = R(H_2O/Fe) \frac{N_{\text{core}}(\text{Fe})}{N_{\text{core}}(\text{C})},$$

where  $R(H_2O/Fe)$  is the molar ratio of H<sub>2</sub>O/Fe in the reaction, and  $N(\text{Fe})_{\text{core}}$  and  $N(\text{C})_{\text{core}}$  are the moles of Fe and C in the core, respectively. We assumed  $R(H_2O/Fe) = 1/3$  (a mole of H<sub>2</sub>O reacts with 3 moles of Fe) based on the reaction  $3\text{Fe} + \text{H}_2\text{O} = 2\text{FeH} + \text{FeO}$ . Then, the equation above can be rewritten as follows:

$$NR(H_2O/C) = R(H_2O/Fe) \frac{X_{\text{core}}(\text{Fe}) \cdot M_{\text{core}}}{m(\text{Fe})} \frac{m(\text{C})}{X_{\text{core}}(\text{C}) \cdot M_{\text{core}}}$$

where  $m(\text{C})$  and  $m(\text{Fe})$  are the molar masses of C and Fe, respectively.  $X_{\text{core}}(\text{C})$  and  $X_{\text{core}}(\text{Fe})$  are the weight fraction of C and Fe in the core, respectively.  $M_{\text{core}}$  is the mass of the core. For  $X_{\text{core}}(\text{C})$ , we used 0.9–2.0 wt% for the carbon content in the outer core (Nakajima et al., 2015; Li et al., 2019). For  $X_{\text{core}}(\text{Fe})$ , 80 wt% was assumed. Using the obtained  $NR(H_2O/C)=2.9\text{--}6.4$ , an annual carbon transfer from the core to the mantle  $F_{\text{CMB}}(\text{C})$  can be estimated from:

$$F_{\text{CMB}}(\text{C}) = m(\text{C}) \frac{f(\text{H}_2\text{O}) \cdot F_{\text{surface}}(\text{H}_2\text{O})}{NR(H_2O/C)}$$

where  $F_{\text{surface}}(\text{H}_2\text{O})$  is the global present-day water flux via subduction into the interior ( $3 \times 10^{12}$  kg/yr or  $1.7 \times 10^{14}$  moles/yr; Cai et al., 2018) and  $f(\text{H}_2\text{O})$  is the water amount reacting with the core at the CMB divided by the water amount subducted at the surface (0–1; we call efficiency term). We obtained  $F_{\text{CMB}}(\text{C})=0.09\text{--}2.1 \times 10^{11}$  kg/yr C for the efficiency of 0.03–0.3 (i.e., 3–30%). Assuming constant water transport to the CMB since subduction initiated (2.5–3.5 Ga; Laurent et al., 2014; Tang et al., 2016; Condie and Kröner, 2008) and that the released carbon remains in the mantle, the total carbon amount added to the mantle  $\Delta X_{\text{mantle}}(\text{C})$  for the time interval  $\Delta t=3$  Ga can be calculated in weight fraction:

$$\Delta X_{\text{mantle}}(\text{C}) = \int_0^{\Delta t} \frac{F_{\text{CMB}}(\text{C})}{M_{\text{mantle}}} dt \approx \frac{\Delta t \cdot F_{\text{CMB}}(\text{C})}{M_{\text{mantle}}}$$

where  $M_{\text{mantle}}$  is the mass of the mantle. We note that time-dependent changes for the terms are assumed to be constant as they are not well known. For example,  $F_{\text{surface}}(\text{H}_2\text{O})$  and  $f(\text{H}_2\text{O})$  would be sensitive to mantle temperature which might have been higher in the past. The results are illustrated in Fig. 2B.

We also estimated the amount of hydrogen incorporated in the core through the water-induced reaction at the CMB. All hydrogen atoms are assumed to alloy with Fe with a 1:1 ratio and be incorporated in the liquid outer core. Therefore, 2 moles of FeH form from a mole of  $\text{H}_2\text{O}$   $R(\text{FeH}/\text{H}_2\text{O}) = 2$ . Then, an annual addition of hydrogen to the core can be expressed as follows:

$$F_{\text{CMB}}(\text{H}) = m(\text{H}) \cdot R(\text{FeH}/\text{H}_2\text{O}) \cdot f(\text{H}_2\text{O}) \cdot F_{\text{surface}}(\text{H}_2\text{O})$$

where  $m(\text{H})$  is the molar mass of hydrogen. Assuming constant water transport to the CMB since initiation of subduction,  $\Delta t = 3$  Ga, and that the incorporated hydrogen remains in the core, the total hydrogen amount added to the core can be calculated in weight fraction:

$$\Delta X_{\text{core}}(\text{H}) = \int_0^{\Delta t} \frac{F_{\text{CMB}}(\text{H})}{X_{\text{core}}(\text{H}) \cdot M_{\text{core}}} dt \approx \frac{\Delta t \cdot F_{\text{CMB}}(\text{H})}{X_{\text{core}}(\text{H}) \cdot M_{\text{core}}}$$

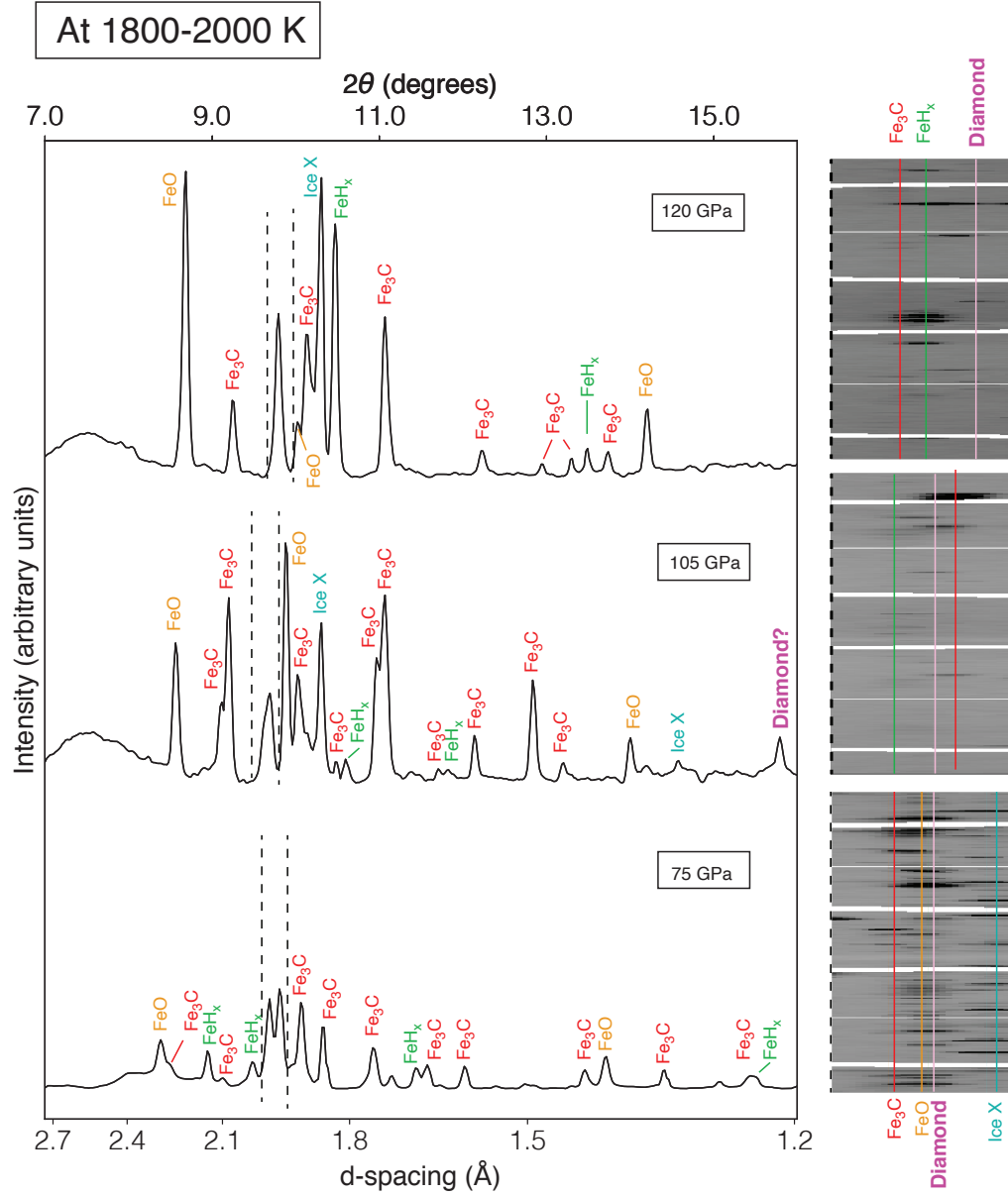
where  $X_{\text{core}}(\text{H})$  is the weight fraction of hydrogen in the present-day outer core (0.3–2.0 wt%; Terasaki et al., 2012; Umemoto and Hirose, 2015; Thompson et al., 2018; Tagawa et al., 2021). The results are illustrated in Fig. 2C.

### Text S3. Reaction efficiency of water at the core-mantle boundary

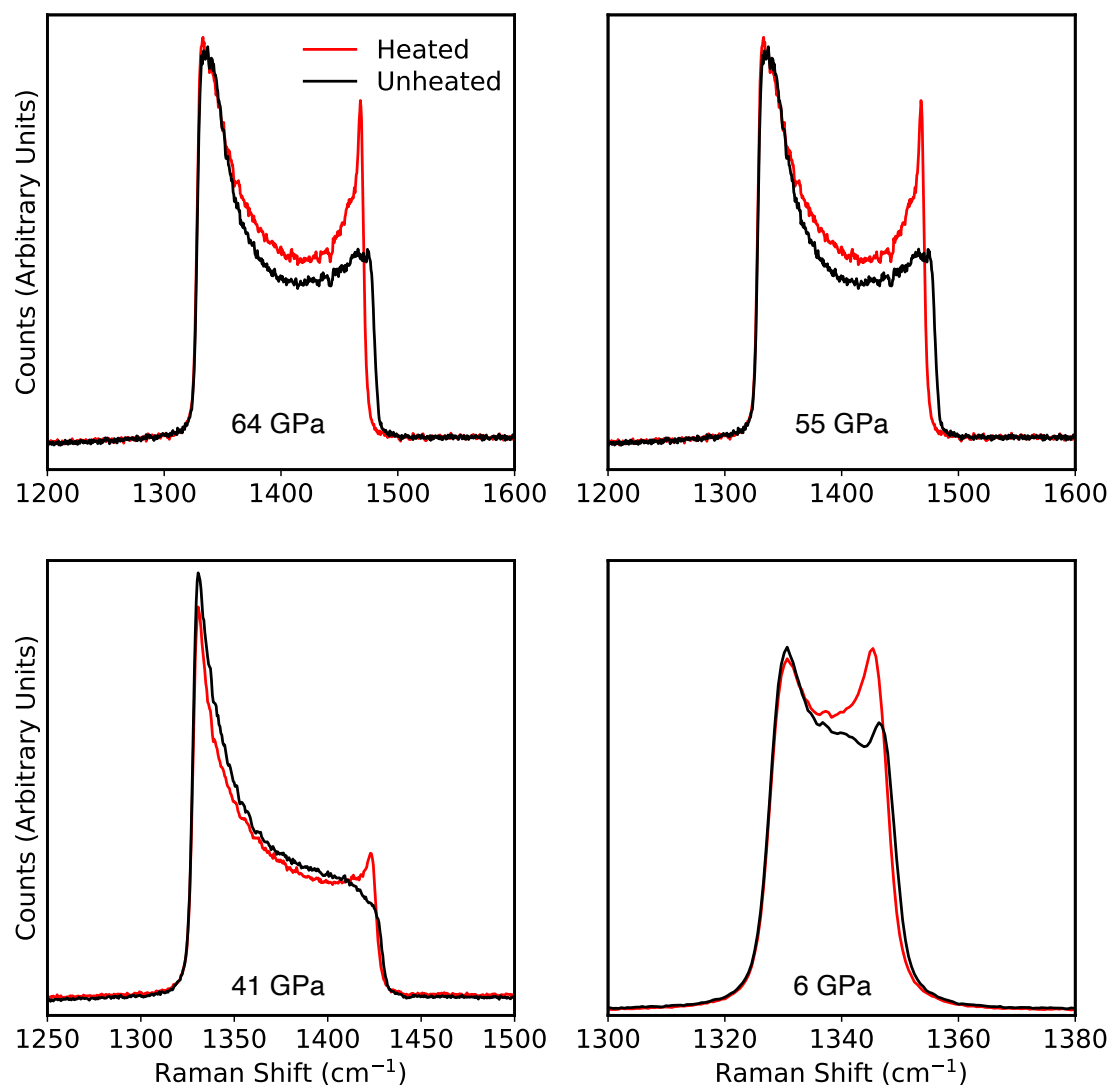
The fraction of water reacting with the core at the CMB relative to the surface water flux into the interior via subduction is highly uncertain. Much of subducted water should be released during its long journey to the CMB. It is likely that most of the water in the crust in subducted slabs is lost in the upper mantle (<300 km depth) because the geotherms of most subducting crusts cross dehydration or melting of hydrous minerals (Okamoto and Maruyama, 2004; Keken et al., 2011). The harzburgitic layer in subducting slabs can still carry a considerable amount of water as its temperature is much cooler than the top layer of subducting slabs (Iwamori, 2004). As a result, only a small fraction of subducted water may be further transported into the deep mantle (e.g., ~32% based on the thermal models of subduction zones from Keken et al., 2011). Hydrous minerals in subducting slabs would undergo another extensive breakdown in the topmost lower mantle (700–800 km depth; Shieh et al., 1998; Nishi et al., 2014).

However, it is possible that a substantial portion of the released water re-hydrates the nominally anhydrous mineral bridgmanite (~0.01 wt%  $\text{H}_2\text{O}$ ) (Fu et al., 2019) in the harzburgitic layer or forms hydrous minerals in the crust, such as phase H (Nishi et al., 2014),  $\text{AlOOH}$  (Piet et al., 2020),  $\text{FeOOH}$  (Nishi et al., 2017), and hydrous  $\text{SiO}_2$  (Nisr et al., 2020). If all the water remained in subducting slabs in the lower mantle was re-hydrated

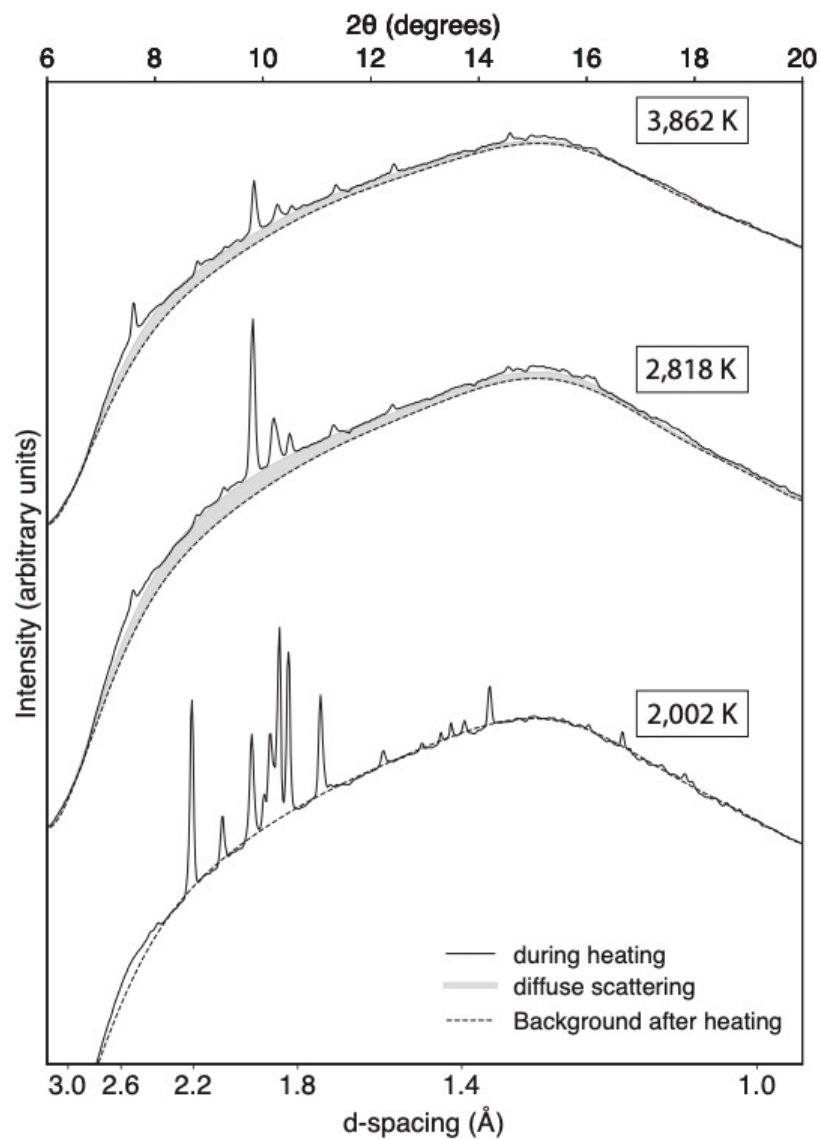
by these hydrous minerals in subducting slabs and eventually participates in the reaction with the outer core at the CMB, the fraction is  $\sim 30\%$ . If the re-hydration process only occurs within the harzburgitic layer in the subducting slabs, the amount of water preserved in slabs is limited to the water solubility of bridgmanite ( $0.01 \text{ wt\% H}_2\text{O}$ ), which is one tenth of the water solubility of ringwoodite ( $\sim 1 \text{ wt\% H}_2\text{O}$ ; Fei and Katsura, 2020). This will lower the fraction an order of magnitude, to  $\sim 3\%$ , even if all the water at the CMB reacts with the outer core. Quantifying how much water arrives at the CMB is difficult because of large uncertainties in dehydration and re-hydration processes in the mantle (Walter, 2021). We assume 3–30% of subducted water may arrive at the CMB. One should be careful to use our estimation because in reality some amount of the water at the CMB could react with the surrounding lowermost mantle instead of the outer core.



**Figure S1** In-situ X-ray diffraction (XRD) patterns of the sample at 75–120 GPa and 1,800–2,000 K in laser-heated diamond anvil cell (LHDAC). X-ray energy was 30 keV. The background is subtracted. The 2-D diffraction images corresponding to the peaks between the dashed lines are shown on the right-hand side. The characteristic line of diamond 111 is observed in the 2-D diffraction images.



**Figure S2** High-pressure Raman spectra of the sample. The sample was synthesized at 71 GPa and 1,800 K. The black spectra were measured at an unheated portion of the sample and the red spectra were measured at the center of heated portion of the sample. The sharp peaks of the red spectra at the edge on the right-hand side are from diamond crystals formed by the reaction between  $\text{Fe}_3\text{C}$  and  $\text{H}_2\text{O}$ .



**Figure S3** In-situ X-ray diffraction (XRD) patterns of the sample at 120-140 GPa and 2,002–3,862 K in laser-heated diamond anvil cell (LHDAC). X-ray energy was 30 keV. The diffuse scattering at 2,818 and 3,862 K indicates melting occurs at those temperatures at 120-140 GPa.