Water-Induced Diamond Formation at Earth's Core-Mantle Boundary

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Abstract The carbon and water cycles in the Earth's interior are linked to key planetary processes, such as mantle melting, degassing, chemical differentiation, and advection. However, the role of water in the carbon exchange between the mantle and core is not well known. Here, we show experimental results of a reaction between Fe, C and H2O at pressures and temperatures of the deep mantle and core-mantle boundary (CMB). The reaction produces diamond, FeO, and FeH2, suggesting that water can liberate carbon from the core in the form of diamond (“core carbon extraction”) while the core gains hydrogen, if subducted water reaches to the CMB. Therefore, Earth's deep water and carbon cycles can be linked. The extracted core carbon can explain a significant amount of the present-day mantle carbon. Also, if diamond can be collected by mantle flow in the region, it can result in unusually high seismic-velocity structures.

Plain Language Summary Carbon plays a vital role in geological processes occurring in the Earth's interior. While most carbon on Earth exists in its core, whether or not the core carbon can be added to the mantle is unclear due to the lack of knowledge of possible carbon transfer mechanism at the core-mantle boundary (CMB). We conducted experiments by reproducing the extreme pressure and temperature conditions of the CMB. Our experiments show that water can react with the metallic iron core and liberate carbon as diamond, suggesting an important relationship between Earth's water and carbon cycles. In addition, our result predicts possible existence of diamond in some regions of the deepest mantle.

1. Introduction

Distribution of carbon in interior provides important clues for understanding the chemical evolution of the Earth. During the accretion, vast majority of Earth's carbon could have been added to the core because of carbon's siderophile nature (Dasgupta et al., 2013; Fischer et al., 2020). The preferential partitioning of carbon into the metallic core predicts a very small amount of residual carbon in the silicate mantle after core formation (1–5 ppm; Dasgupta et al., 2013). However, the estimated carbon abundance in the present-day mantle is much greater (~120 ppm for pyrolite; McDonough & Sun, 1995). It remains unclear how the mantle has gained much more carbon (Dasgupta et al., 2013).

Several models have been proposed to explain the present-day mantle inventory of carbon. For example, the additional carbon might have been delivered through a volatile-rich late veneer that occurred after core formation (Wänke, 1981). This model has difficulties explaining the difference in carbon isotopic composition between CI chondritic materials and the average mantle (Deines, 2002; Kerridge, 1985) and the superchondritic H/C ratio of the bulk silicate Earth in present day (Hirschmann & Dasgupta, 2009). Alternatively, carbon ingassing might have occurred after core formation. Carbon in an early atmosphere might have dissolved into an early magma ocean and precipitated graphite, diamond, or carbide, increasing the amount of the mantle carbon (Dasgupta et al., 2013). Also, some amount of carbon-bearing metallic melts might have been trapped in the mantle if incomplete segregation of metallic liquid from the mantle occurred during core formation (Dasgupta et al., 2013). A recent study proposed graphite floatation on a magma ocean as another mechanism for core carbon loss (Kepler & Golabek, 2019).

The core is the largest carbon reservoir within the Earth (McDonough, 2003), although estimates of the amount of carbon in the core vary, for example, between 0.09 and 4 wt% (Dasgupta & Walker, 2008; Dasgupta et al., 2013;
Fischer et al., 2020; McDonough, 2003; Wood et al., 2013). Therefore, core carbon loss to the mantle through the core-mantle boundary (CMB) chemical reactions after core formation could be a viable source for the observed excess mantle carbon. Dasgupta et al. (2013) predicted that if deeply subducted hydrous minerals break down and release water at the CMB, water may react with the iron core. They further speculated that the reaction would form FeHx and liberate carbon from the iron core by forming CO, COx, or FeCOx. This hypothesis suggests that Earth’s carbon, hydrogen, and water cycles may be linked at the CMB. Experiments have demonstrated the plausibility of hydrous minerals in subducting slabs, such as AIOOH (Piet et al., 2020), FeOOH (Nishi et al., 2017), phase H (Nishi et al., 2014), and hydrous SiO2 (Lin et al., 2020; Nisr et al., 2020). Thus, subduction processes can result in the transport and release of water in the deepest mantle, although dehydration processes at the CMB could be more complicated than what has been observed in experiments on simplified chemical systems.

H, O, and C are all light element candidates for the core (e.g., Hirose et al., 2013), which could affect one another’s solubility in the region. Experiments showed that CxHy(2n+2) paraffin reacts with Fe and forms FexC, which was then replaced by FeHx + diamond at 64 GPa and 1650 K (Narygina et al., 2011) and up to 127 GPa and >2100 K (Hirose et al., 2019). Hirose et al. (2019) also showed that the same reaction occurs even with liquid Fe at 58–66 GPa and 3220–3710 K. It thus appears that hydrogen’s strong affinity to iron could lower the solubility of C in the core. However, whether iron carbide directly react with water to liberate carbon at pressure and temperature (P–T) conditions relevant to the CMB has never been tested by experiments. In order to understand the possibility of carbon exchange between the core and the mantle induced by the presence of water at the CMB, we conducted experiments on reactions between iron carbide (FeC) and water (H2O) at 70–140 GPa and up to 4050 K (thus bracketing the CMB pressure of 136 GPa) using in situ X-ray diffraction (XRD) in laser-heated diamond anvil cells (LHDACs). The experiments found formation of diamond from reaction between iron carbide and water, opening up a possibility for the chemical exchange between the core and the mantle.

2. Materials and Methods

FeC was synthesized at high pressures using the multi-anvil press at the University of Hawaii at Manoa. The starting material was a mixture of Fe powder (99.9+% purity, Aldrich Chemical Company) and graphite powder (99.9995% purity, Alfa Aesar Company) with an atomic ratio Fe:C = 3:1. The mixture was loaded into a MgO capsule of an 18/12 multi-anvil cell assembly, which was then compressed to 3 GPa and heated at 1300 K for 8 hr to synthesize FeC. The FeC sample was then analyzed by electron microprobe to confirm its purity and composition. The synthesized FeC was loaded as ~10 μm-thick foils in symmetric-type LHDACs with 150 and 200 μm-sized culets using a micro-manipulator (Microsupport Axis Pro SS) at Arizona State University (ASU). Distilled water was loaded as a pressure medium.

In situ X-ray diffraction (XRD) experiments (Table 1) were conducted at sector 13-IDD of the GeoSoilEnviroConsortium (GSECARS) in the Advanced Photon Source (APS; Prakapenka et al., 2008). X-ray energy was 30 keV. X-ray diffraction images were collected using a Dectris Pilatus detector and analyzed using DIOPTAS (Prescher & Prakapenka, 2015) and PeakPo (Shim, 2017). The exposure time was 5–10 s. Typical X-ray and laser beam diameters were ~5 and 20 μm, respectively. The heating was conducted with a pre-set laser power which was directly applied at the start of the heating and maintained for 5 s each heating cycle. This heating method reduces the risk of overheating the diamond anvils particularly with water as a pressure medium, preventing LHDACs from failure during high-temperature heating. For temperature estimations, we fit the thermal radiation spectra measured from both sides of the sample to a Planck gray-body equation for estimation of temperature. The temperature uncertainty is estimated (Table 1) considering the temperature reading difference between the two sides of the sample and the intrinsic uncertainty from the spectroradiometry (~100 K; Prakapenka et al., 2008).

At relatively low temperatures (<2200 K), pressure was estimated using the equation of state (EOS) parameters of FeO in the NaCl-type structure (Fischer et al., 2011). At higher temperatures (>2700 K) for Sample #3 (Table 1), reliable pressures were difficult to estimate, unlike at the lower temperatures where diffraction lines of FeO are robustly observed. In this case, pressure was estimated from the EOS of diamond (Dewaele et al., 2008) based on its 111 peak position, which was identified more clearly than at lower temperatures. The calculations yield pressures up to 140 GPa (Table 1). The calculated pressures using the diamond at 2000 K agree within 0.2%–1.3% with those estimated using the NaCl-type FeO in the same heating spot in Sample #3. Given the fact that pressures of some runs are estimated from a single diffraction line, we assigned a conservative uncertainty (10%) for the
pressures at temperatures over 2700 K. The samples could not be recovered to room conditions because of failure of the diamond anvils during decompression or sample loss when H₂O converts to liquid during decompression to ∼1 bar.

Micro-Raman measurements were conducted for identifying diamond in Sample #1 at high pressures. A solid-state (frequency doubled Nd:YAG) laser was used with a 532 nm monochromatic beam at ASU. The laser power at the sample was ∼3 mW. The spectrometer was calibrated using the neon emission spectra. Measurements were conducted using an 1,800 grooves/mm grating. We calibrated pixel-to-pixel sensitivity differences in the charge-coupled device (CCD) detector using the spectrum of a glass with well-known fluorescence intensities at different wavenumbers. The exposure time for each spectrum measurement was 1–10 s. Pressure was determined using a diamond Raman gauge (Akahama & Kawamura, 2006).

### 3. Results

XRD peaks of Fe₃C and ice X were confirmed at high pressures before laser heating. The diffraction peaks were broad because of differential stress. After laser heating of the samples, we found two sets of mineral assemblages depending on heating temperature. At lower temperatures of 1700–2200 K at 71–127 GPa (Samples #1 and 2; Table 1), we observed the diffraction peaks of FeO (NaCl-type, B1), dhcp-FeHₓ, and possibly diamond (Figure 1a and Figure S1 in Supporting Information S1). Some XRD patterns show fcc-FeHₓ as an additional phase with relatively weak peak intensities (Table 1). The diffraction peaks of Fe₃C were also observed as sharp peaks. The characteristic diffraction line of diamond 111 was difficult to separate from that of dhcp-FeHₓ 004. A run at 120 GPa and 2002 K showed a clear diamond peak at 2θ ∼16°, which can be indexed as the 022 line (Figure 1a).

We further examined the sample synthesized at ∼72 GPa and ∼1800 K using Raman spectroscopy (Sample #1; Table 1). In order to reduce the signal from the diamond anvils and enhance the signal from diamond formed from the reaction in the sample, we used the confocal micro-Raman technique which blocks out-of-focus light in signal detection. Because the expected depth resolution is still greater than the thickness of the sample (∼8 μm) at high pressure, signals from the diamond anvils were observed. The strong peak at 1,320 cm⁻¹ is from the uncompressed part of the diamond anvils (Figure 1b). The right-hand side of the peak extends up to 1,470 cm⁻¹, which

| Sample #  | P (GPa)     | T (K)      | Phase assemblage            | Vₑₒ(A³)   | V₅diamond (A³) |
|-----------|-------------|------------|-----------------------------|-----------|----------------|
| Sample #1 | 71–74(8)    | 1700–1900(141) | Fe₃C, FeO, d,f-FeHₓ, C     | 62.68(4)  |                |
| Sample #2 | 92(8)       | 2000(180)  | Fe₃C, FeO, d,f-FeHₓ, C     | 59.58(1)  |                |
| Sample #3 | 120(8)      | 2002(157)  | Fe₃C, FeO, d,f-FeHₓ, C     | 55.96(1)  | 38.0(4)        |
|           | 120(8)      | 1998(165)  | Fe₃C, FeO, d,f-FeHₓ, C     | 56.02(1)  | 38.0(4)        |
|           | 125(13)     | 2723(100)  | py, f-FeHₓ, C, *           | 38.1(4)   |                |
|           | 126(13)     | 2758(124)  | py, f-FeHₓ, C, *           | 38.0(4)   |                |
|           | 133(13)     | 2818(126)  | py, f-FeHₓ, C, *           | 37.8(4)   |                |
|           | 130(13)     | 2970(177)  | py, f-FeHₓ, C, *           | 38.0(4)   |                |
|           | 131(13)     | 3332(396)  | py, f-FeHₓ, C, *           | 38.0(4)   |                |
|           | 138(14)     | 3862(146)  | py, f-FeHₓ, C, *           | 37.9(4)   |                |
|           | 140(14)     | 4051(554)  | py, f-FeHₓ, C, *           | 37.9(4)   |                |

*Note. Pressure was calculated based on unit-cell volume (V) of diamond (B1) or FeO (B1) by using their equation of state parameters (Dewaele et al., 2008; Fischer et al., 2011). Temperature uncertainties are estimated to be <200 K. dhcp-FeHₓ, C: diamond, f-FeHₓ: fcc-FeHₓ, py: pyrite-type FeO₂Hₓ. *: X-ray diffraction lines which can be assigned to either dhcp-FeHₓ or tetragonal FeH₂.

*Pressure and temperature were maintained in the ranges throughout the sample. *Temperature was increased at the same spot over the runs.
is from the compressed part of the diamond anvils. Because the diamond inside the sample is at a higher pressure than diamond anvil, the peak would appear at the end of the spectral feature (∼1,470 cm⁻¹; Boppart et al., 1985). The heated areas clearly showed a sharp peak at the edge of the spectral feature, whereas the unheated areas do not show such a peak (Figure 1b), demonstrating the existence of diamond formed from the reaction between Fe₃C and H₂O. Raman spectra measured during decompression also showed the consistent results at 64, 55, 41, and 6 GPa (Figure S2 in Supporting Information S1). At a temperature range of 1700–2200 K, the reaction can be summarized as:

\[ \text{Fe}_3\text{C} + \text{H}_2\text{O} \rightarrow \text{FeO} + 2\text{FeH} (\text{dhcp}) + \text{C (diamond)} \]

At higher temperatures of 2700–4050 K (Sample #3), we observed the formation of pyrite-type FeOOHₙ, fcc-FeHₓ, and diamond at 125–140 GPa (Figure 1a). The diffraction lines of py-FeOOHₙ and fcc-FeHₓ are robustly observed. There are two unassigned diffraction peaks with weak intensities (labeled with "*" in Figure 1a), which can be indexed with either dhcp-FeHₓ or FeH₂ (Figure 1a). In either case, it is likely that the thermal gradient during laser heating promoted an appearance of additional iron hydride as a minor phase.

At 3860 K, the diffraction patterns remain similar to those measured at 2720 K (Figure 1a), but with stronger intensity in general, suggesting higher degree of reaction. The observation of diffraction lines for ice X is likely due to the axial thermal gradients as H₂O should be molten if excess H₂O exists (Schwager et al., 2004). Similarly,
we infer that the diffraction lines of py-FeOOH$_4$ came from the cooler sample regions along the axial thermal gradients because its dehydration temperature is lower (Nishi et al., 2017) than the heating temperatures. We observed diffuse scattering in the diffraction patterns at temperatures over 2700 K (Figure S3 in Supporting Information S1) caused by melting. Temperatures greater than 2700 K at 120–140 GPa are higher than the reported solidus of Fe,C (Mashino et al., 2019), as well as the extrapolated solidus of FeH$_4$ (Sakamaki et al., 2009). Therefore, the metallic melt should be rich in H at the heating center. Diamond should be stable under the studied $P$–$T$ conditions because of its extremely high melting temperature ($\sim$7000 K at 130 GPa; Wang et al., 2005) as observed in both XRD patterns and Raman spectra.

**4. Discussion**

**4.1. Chemical Exchange Between the Mantle and Core**

Previous experiments using paraffin + Fe metal starting materials showed that H is more siderophile than C, forming diamond at lower-mantle conditions (Hirose et al., 2019; Narygina et al., 2011), although it remains unclear that the reduced hydrogen can be provided to the lower mantle (Hu et al., 2016; Nishi et al., 2017). Recent melting experiments on Fe-C-H alloys up to 70 GPa (Lai et al., 2022) also observed diamond due to a substitution of C by H.

In our experiments of Fe,C + H$_2$O, similar partitioning behaviors of H and C were observed, which resulted in the formation of diamond although there might have been a trace amount of carbon remaining in iron alloys after reaction. The observation of FeO and FeH$_4$ in our experiments with excess water is consistent with previous experiments of 2Fe + H$_2$O = FeO + 2FeH with less water (6 wt% H$_2$O) at similar pressures and temperatures ($\sim$120 GPa and 2000–2250 K; Nishi et al., 2020). Also, the decomposition of H$_2$O at the CMB shown in this study agrees well with other experiments (Mao et al., 2017; Yuan et al., 2018). The consistency of the reaction products between previous experiments and ours supports that the observed phases in this study are stable likely because of the suppression of kinetic effects by hydrogen and the simple chemistry system of the starting material (Fe-C-H-O).

This study demonstrates that not only water can play a critical role in chemical exchange between the mantle and the core, but also Earth's carbon cycle is closely linked to the H and O cycles. Our results indicate that if H$_2$O reacts with liquid iron metal at CMB conditions, metallic melt (rich in Fe and H) would form and most likely be incorporated into the liquid outer core (Figure 2a). Some amount of O would remain in the mantle as iron oxide (FeO), while the metallic melt may also incorporate O.

The water released from the dehydration of hydrous minerals in subducting slabs may have been a continuous process from when the hydrated slabs first reached the CMB following the initiation of plate tectonics. Although the timing of the onset of subduction is not well constrained, studies indicate that subduction might have initiated 2.5–3.5 Ga (Condie & Kröner, 2008; Laurent et al., 2014; Tang et al., 2016). Theoretical and experimental studies have suggested that subducting slabs would have been negatively buoyant in the transition zone and the topmost lower mantle since subduction initiated, thus promoting their descent to the deep lower mantle (Klein et al., 2017; Ko et al., 2020). If water in subducting slabs has been transported to the CMB and released in the region for $\sim$3 billion years, the core-mantle chemical exchange presented here may have occurred during the time.

The carbon transfer from the core to the mantle results in the gradual augmentation of the mantle carbon for a significant part of the Earth’s history. This is consistent with the earlier hypothesis that water may facilitate carbon transfer at the CMB by Dasgupta et al. (2013), which may account for the present-day mantle carbon content (e.g., 120 ppm C; McDonough & Sun, 1995). However, the present study suggests a form of carbon produced from the CMB reaction is diamond, different from the oxidized carbon assumed by Dasgupta et al. (2013). Carbonate
The amount of core carbon added to the mantle by the water-induced reaction at the CMB (after core formation) can be estimated. Efficiency of the reaction was defined as the water amount participating in the reaction at the CMB divided by the water amount subducted at the Earth's surface (see Supplementary information for detail). It should be noted that how much subducted water reaches the CMB is poorly constrained because of large uncertainties in dehydration and re-hydration processes in the mantle (Walter, 2021). In this estimation, a constant rate of water transport was assumed via subduction from the surface (3 × 10^{12} kg/yr H_{2}O for the global water flux at the surface in present day; Cai et al., 2018) for 3 Ga. Also, we assumed a constant carbon content in the outer core (0.9–2.0 wt%; Li et al., 2019; Nakajima et al., 2015). If 3–30% of subducted water reaches the CMB and reacts with the core (see Supplementary Information for detail), 7–160 ppm C can be added to the mantle over 3 Ga after core formation. However, it should be noted that these values are likely overestimated because only a portion of the released water from subducting slabs would react with the outer core, while the rest would react with the surrounding lower mantle.

The proposed model has the potential to account for a substantial portion of the present-day carbon in the mantle. For example, 120 ppm of the present-day carbon content (McDonough & Sun, 1995) can be explained solely by the water-induced carbon transfer from the core (Figure 2b), if water has been efficiently transported to the CMB over the last 3 Ga. Yet, this calculated “core carbon extraction” is only 0.2%–1.7% (0.3–6.3 × 10^{20} kg C) of the estimated carbon content of the present-day outer core (Li et al., 2019; Nakajima et al., 2015). Therefore, most of the core carbon incorporated during its formation would still remain there. In addition, the model can estimate the amount of hydrogen added to the core through the water-induced reaction. If hydrogen alloys with iron metal with a 1:1 molar ratio (Supplementary Information), for the above assumed water transport efficiency for the core carbon extraction, our calculation predicts that the amount of hydrogen added to the outer core (0.3–3.0 × 10^{20} kg H) accounts for only 0.1%–5.3% of the estimated present-day core hydrogen (Tagawa et al., 2021; Terasaki et al., 2012; Thompson et al., 2018; Umemoto & Hirose, 2015, Figure 2c). Therefore, the core's carbon and hydrogen budgets would not be altered significantly by the core carbon extraction and are mainly determined during core formation.

### 4.2. Seismic Implications

Diamond formed at the CMB is expected to be advected by mantle flow, ultimately entrained by upwelling mantle currents. This process is facilitated by the anomalously low density of diamond (32% lower than the surrounding mantle). Therefore, diamond residency at the CMB may be limited, but small-scale convection on the CMB may lead to temporary localized accumulations of diamonds in regions strongly affected by subducted slabs in the lowermost mantle (Li, 2020; Solomatov & Moresi, 2002). Thus, regions with diamonds may not be ubiquitous at the CMB, but we expect their presence in CMB regions of deeply subducting hydrated slabs.

A question pertains whether the lowermost mantle diamond can be advected by upwelling mantle to the uppermost mantle. Diamond may react with metallic iron in the lower mantle since the major minerals in the lower mantle are known to have a limited carbon solubility (Shcheka et al., 2006). The reaction may form iron carbide during ascent, but diamond can coexist with Fe₃C if the carbon proportion is over 8 wt% (Lord et al., 2009). The upwelling flow would undergo an inevitable redox change when passing the 660-km discontinuity where Fe^{3+}-rich bridgmanite is destabilized and diamond is oxidized to carbonatite melts (Rohrbach & Schmidt, 2011) although the degree of which for this process may depend on the oxygen fugacity change across the transition zone. Such a redox change would make the upwelling of the lowermost mantle diamond to the uppermost mantle difficult. However, the carbonatite melt can still carry information about other minerals entrained together with the diamond from the CMB. If the melt solidifies new diamond that is sent to the surface, diamond inclusions can exhibit geochemical signatures of their deep origin. Some diamond inclusions show low Mg# (0.2–0.6) in magnesiowüstite (Harte & Hudson, 2013; Hayman et al., 2005; Kaminsky et al., 2009; Wirth et al., 2014) and an association of iron carbide and diamond (Kaminsky & Wirth, 2011), suggesting their possible origin at the CMB, as advocated in this study.

Diamond exhibits higher bulk and shear moduli as well as lower density compared to major mantle minerals (Núñez Valdez et al., 2012): 50%–72% and 74%–110% higher $\rho$, and S wave velocities, respectively, than pyrolite.
in the lower mantle. We calculated the seismic velocities and density for the mineral assemblage of pyrolite + diamond with varying diamond proportion (0–20 wt%) at the CMB conditions (136 GPa and 2500–4000 K) using the Perple_X thermodynamic modeling program (Connolly, 2009) with the SBL2011 data set (Stixrude & Lithgow-Bertelloni, 2011) and elastic properties of diamond (Dewaele et al., 2008; Núñez Valdez et al., 2012). The calculation demonstrates that even a small amount of diamond mixed with the background mantle can dramatically decrease density and increase seismic velocities at the CMB (Figure 3). Therefore, if diamond-bearing structures exist at the CMB, their exceptionally fast velocities could be detectable in seismic studies. Considering the fact that less dense structures could have longer resident time in regions with strong downwelling flow, the high velocity structures could be found in regions associated with subducting slabs in the lowermost mantle.

5. Conclusions
We conducted experiments on reaction between Fe,C and H2O using LHDACs combined with in situ X-ray diffraction at 70–140 GPa and up to 4050 K. We found that the reaction liberates carbon in the form of diamond as hydrogen and oxygen alloy with iron. This result implies that the Earth’s core carbon may have been transferred to the mantle if subducted water has reacted with the core. Our model provides a testable prediction in that such diamonds, if locally collected by mantle flow, lead to small-scale high velocity structures near the subducted materials at the CMB.

Data Availability Statement
Datasets for this research are available online (https://doi.org/10.5281/zenodo.6040059).

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