Carbon isotopic signatures of super-deep diamonds mediated by iron redox chemistry


Abstract

Among redox sensitive elements, carbon is particularly important because it may have been a driver rather than a passive recorder of Earth’s redox evolution. The extent to which the isotopic composition of carbon records the redox processes that shaped the Earth is still debated. In particular, the highly reduced deep mantle may be metal-saturated, however, it is still unclear how the presence of metallic phases influences the carbon isotopic compositions of super-deep diamonds. Here we report ab initio results for the vibrational properties of carbon in carbonates, diamond, and Fe3C under pressure and temperature conditions relevant to super-deep diamond formation. Previous work on this question neglected the effect of pressure on the equilibrium carbon isotopic fractionation between diamond and Fe3C but our calculations show that this assumption overestimates the fractionation by a factor of ~1.3. Our calculated probability density functions for the carbon isotopic compositions of super-deep diamonds derived from metallic melt can readily explain the very light carbon isotopic compositions observed in some super-deep diamonds. Our results therefore support the view that metallic phases are present during the formation of super-deep diamonds in the mantle below ~250 km.

Introduction

Diamonds are prime recorders of the carbon isotopic compositions of the Earth because some of them are sourced deeply from the longest, isolated regions of Earth’s mantle (Cartigny et al., 2014). The $\delta^{13}$C values (deviations in per mille of $^{13}$C/$^{12}$C ratios relative to V-PDB) of natural diamonds show a broad range of variations from ~-41 ‰ to +3 ‰ with a mode at -5 ± 3 ‰ (Cartigny et al., 2014). Of particular interests are very low $\delta^{13}$C values of -26 ‰ to -41 ‰ found in some eclogitic and super-deep diamonds (e.g., De Stefano et al., 2009; Smart et al., 2011; Smith et al., 2016). These low $\delta^{13}$C values are most commonly found in eclogitic diamonds (e.g., Walter et al., 2011), which presumably incorporated a recycled oceanic crust component. It is thus unlikely that these $\delta^{13}$C values were inherited from Earth’s primordial materials. Although eclogitic diamonds with lowest $\delta^{13}$C values may originate from organic matter at 2.0-2.7 Ga ($\delta^{13}$C ~ -40 ‰ to -60 ‰) (Smart et al., 2011), such organic matter unlikely survives at the depths (300-1000 km) where super-deep diamonds form (e.g., Anzolini et al., 2019). Isotopic fractionation associated with diamond precipitation from either CH4 or CO2-bearing fluids (Galimov, 1991) is also an unlikely explanation for the most negative $\delta^{13}$C values measured in these diamonds. The reasons are that: (1) the equilibrium fractionation between diamond and CH4 at mantle temperatures (~+1 ‰) is too low to drive the residual fluid to very negative $\delta^{13}$C values by Rayleigh distillation; (2) the fractionation between diamond and CO2 of ~ -3 ‰ at mantle temperatures could only produce diamonds whose $\delta^{13}$C values are ~ -8 ‰ or higher. Overall, the question of how some super-deep diamonds acquired highly negative $\delta^{13}$C values is still open.

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Through plate tectonics, relatively oxidised iron and carbon species at the Earth’s surface are transported to the deep mantle by subducted slabs, where Fe$^{3+}$ can disproportionate into Fe$^{3+}$ and metallic Fe (Equation 1) below ~250 km due to stabilisation of Fe$^{3+}$ in garnet, pyroxene and bridgmanite (Frost et al., 2004; Rohrbach et al., 2007):

$$\text{3FeO} = \text{Fe} + \text{Fe}_2\text{O}_3 \quad \text{Eq. 1}$$

The resulting metallic Fe would react with carbonates to form either diamond (Equation 2) or iron carbide (Equation 3), depending on the local Fe-C ratio and thus redox state (Palyanov et al., 2013):

$$\text{FeCO}_3 + 2\text{Fe} = 3\text{FeO} + \text{C} \quad \text{Eq. 2}$$

$$\text{Fe}_3\text{O}_4 + 5\text{Fe} = 3\text{FeO} + \text{Fe}_2\text{C} \quad \text{Eq. 3}$$

FeC can also serve as a reduced C source to form diamonds through the following redox reaction (Bataleva et al., 2016):

$$\text{Fe}_2\text{C} + 3\text{Fe}_2\text{O}_3 = 9\text{FeO} + \text{C} \quad \text{Eq. 4}$$

Moreover, Fe-C alloys/ mixtures may melt under the pressure and temperature (P-T) conditions of the mantle because of their relatively low melting temperatures, especially in the presence of Ni, as compared to other mantle minerals (e.g., Rohrbach et al., 2014; Liu et al., 2016). The resultant Fe-C melt can form diamonds through the reaction mediated by iron redox chemistry:

$$\text{Fe-C melt} + \text{Fe}_2\text{O}_3 = 3\text{FeO} + \text{C} \quad \text{Eq. 5}$$

The presence of S or other light elements can significantly lower C solubility in metallic melt and therefore promote diamond formation (Bataleva et al., 2015). For example, Fe-Ni-S-C inclusions have been found in super-deep diamonds (e.g., Kaminsky and Wirth, 2011; Smith et al., 2016). Finding such metallic inclusions requires careful examination as these inclusions are small in size (µm to nm scale) and can be mistaken for graphite (Kaminsky and Wirth, 2011; Smith et al., 2016). The presence of metallic inclusions supports the view that C-bearing metallic melt could serve as a carbon source for some super-deep diamonds below ~250 km.

Horita and Polyakov (2015) have attempted to address the aforementioned question through calculations of the reduced partition function ratio (β-factor) of C in Fe$_2$C using the heat capacity and the iron phonon density of states (PDOS) at 1 bar. They combined this β-factor with previously published β-factors of diamond and carbonates to calculate the carbon equilibrium isotopic fractionation $\Delta^{13}C$ between these phases, $\Delta^{13}C_{\text{B-A}} = 1000(\ln \beta_{\text{B}} - \ln \beta_{\text{A}})$ (Eq. 6), where B and A are two phases in isotopic equilibrium. An important assumption that Horita and Polyakov (2015) made is that pressure has no effect on this fractionation. However, super-deep diamonds form under high P-T conditions in the mantle below 250 km depth, and applied pressure has undoubtedly been shown to stiffen lattice bonds and induce structural and electronic transitions, which in turn can affect β-factors of C in host phases (e.g., Lin et al., 2004, 2012). In order to constrain reliably the extent of C isotopic fractionation during super-deep diamond formation, we used DFT augmented by a Hubbard U correction method (Giannozzi et al., 2009) to calculate the β-factors of C in MgCO$_3$, FeCO$_3$, Fe$_2$C and diamond (Tables S-1, S-2) at the P-T conditions of subducted slabs in the mantle. We also measured the PDOS of Fe$^{2+}$ in FeCO$_3$ by nuclear resonant inelastic X-ray scattering (NRIXS) spectroscopy (Dauphas et al., 2018) to evaluate the accuracy of the theoretical calculations.

### PDOS of Fe and C in Minerals Relevant to Diamond Formation

The DFT + U calculation was verified by comparing the theoretical PDOS of Fe$^{2+}$ in FeCO$_3$ with the one measured by NRIXS (Fig. 1). The PDOS results in theory and experiment match well with each other, which could also support the validity of the calculated β-factors of C in carbonates, diamond and nonmagnetic Fe$_2$C (Fig. S-1). Synchrotron Mössbauer spectra (Fig. S-2) and optical images (Fig. S-3) show that the spin transition of Fe$^{2+}$ in FeCO$_3$ occurs between 44-46 GPa at 300 K. Across the spin transition, the unit cell volume collapses by 9.4 %, the Fe-O bond length is shortened by 4.8 % (Fig. S-4). Meanwhile, the spin transition of iron results in ~5 % decrease of the β-factor of C in LS FeCO$_3$ compared to its HS state (Fig. S-5) as the C-O bond length is lengthened by 2.1 % (Fig. S-5). The magnetic state of Fe$_2$C changes from ferromagnetic at ambient condition to paramagnetic and finally nonmagnetic at pressures higher than ~22-60 GPa (Lin et al., 2004; Gao et al., 2008). Therefore, nonmagnetic Fe$_2$C is the relevant phase for most mantle depths. Similar to previous theoretical calculations (Horita and Polyakov, 2015) and C isotopic measurements on natural diamonds and iron carbide inclusions (Mikhail et al., 2014), the magnitude of $\Delta^{13}C_{\text{Dia-FeC}}$ is larger than other inter-mineral fractionations involving diamond, such as $\Delta^{13}C_{\text{Dia-Carbonates}}$ (Fig. S-6). Our calculated $\Delta^{13}C_{\text{Dia-FeC}}$ values along the representative P-T conditions of modern mantle and cold slab (Fig. S-6) are as much as 27 % lower than the 1-bar value of $\Delta^{13}C_{\text{Dia-FeC}}$ reported by Horita and Polyakov (2015). Therefore the 1-bar data would overestimate the C isotopic fractionation during diamond formation from a Fe$_2$C source under mantle P-T conditions.

### Carbon Isotopic Fractionation in Diamonds through Redox Reactions

As discussed by Horita and Polyakov (2015), the most significant reaction that can impart C isotopic fractionation to diamonds is one involving the oxidation of C alloyed with metallic melt to release C to form diamonds (Equation 5). To assess how redox reactions involving Fe-C melt below ~250 km can influence the $\delta^{13}C$ values of super-deep diamonds, we modelled the isotopic fractionation of C between diamond and Fe-C melt. Our calculations accounting for various P-T and compositional factors allow us to test whether this diamond formation pathway can account for their $\delta^{13}C$ values.

The C isotopic fractionation can be modelled by using a Rayleigh distillation if the diamonds produced do not back-react with the C source, which is reasonable if the Fe-C source is a melt and the reaction product is a solid characterised by a low self-diffusivity (Koga et al., 2005). As it is challenging to calculate the β-factor of C in Fe-C melt directly, $\Delta^{13}C_{\text{Dia-FeC melt}}$ is calculated by the sum of $\Delta^{13}C_{\text{Dia-FeC}}$ (Fig. S-6) and the equilibrium fractionation $\Delta^{13}C_{\text{FeC melt}} = -5.6 \times 10^9 T^2$ anchored to the experimentally determined value of ~2 % at 6.3 GPa and 1673 K (Reutsky et al., 2015). By using this calculated $\Delta^{13}C_{\text{Dia-FeC melt}}$, $\delta^{13}C$ values of diamonds forming from metallic melt can be calculated using a Rayleigh distillation model. Relative to the Fe-C melt source, the diamonds are enriched in the heavy isotope of C. Removal of isotopically heavy diamonds would have driven the Fe-C melt reservoir towards lower $\delta^{13}C$ values and diamonds formed from this low $\delta^{13}C$ reservoir progressively acquired more negative $\delta^{13}C$ values.

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Ref: Horita and Polyakov (2015)
The probability density function (PDF) of $\delta^{13}C_{\text{Dia}}$ values of diamond formed from metallic melt, which we note as $g(\delta^{13}C_{\text{Dia}})$, is simply given as below (see detailed derivation in Supplementary Information),

$$g(\delta^{13}C_{\text{Dia}}) = 1/\Delta^{13}C_{\text{Dia-Source}} \exp[-(\delta^{13}C_{\text{Dia}} - \delta^{13}C_{\text{Source}})/\Delta^{13}C_{\text{Dia-Source}} - 1]$$

The PDFs for $\Delta^{13}C_{\text{Dia-FeC}}$ at representative upper mantle, transition zone, and lower mantle depths are shown in Figure 2. For each PDF, $\Delta^{13}C_{\text{Source}}$ is set to locate the maximum probability of $\Delta^{13}C_{\text{Dia}}$ at -5‰, which is the mode of $\delta^{13}C$ of worldwide diamonds (Cartigny et al., 2014). Because of the decrease of $\Delta^{13}C_{\text{Dia-FeC}}$ melt with increasing depth and temperature, the extent of the negative tail of each PDF decreases with depth where diamonds form (Fig. 2). For example, the cumulative probability of $\Delta^{13}C_{\text{Dia}}$ values lower than -26‰ is ~0.17 at 250 km, and it decreases to 0.10 and 0.05 at 660 and 1500 km depths, respectively (Fig. S-7). This shows that super-deep diamonds with very light C isotope could have formed from C-bearing metallic melt in the reduced part (>250 km) of the upper mantle.

**Conclusion**

By using the $\beta$-factors of carbon in relevant minerals/melt, the carbon isotopic fractionations between carbon-bearing phases possibly involved in super-deep diamond formation are calculated. The corresponding PDFs for $\delta^{13}C$ of super-deep diamonds from different carbon sources are derived. Based on the comparison between the histogram for $\delta^{13}C$ of super-deep diamonds and the derived PDFs, super-deep diamonds could crystallise from C-saturated metallic melt, thus supporting the existence of a deep mantle saturated in metallic iron.
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Author Contributions


Additional Information

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