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

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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.

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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 δ^{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 δ^{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 δ^{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 δ^{13} C values were inherited from Earth's primordial materials. Although eclogitic diamonds with lowest δ^{13} C values may originate from organic matter at 2.0-2.7 Ga (δ^{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 δ^{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 δ^{13} C values by Rayleigh distillation; (2) the fractionation between diamond and CO₂ of ~-3 ‰ at mantle temperatures could only produce diamonds whose δ^{13} C values are ~-8 ‰ or higher. Overall, the question of how some super-deep diamonds acquired highly negative δ^{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^{2+} 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):

$$3FeO = Fe + Fe_2O_3$$
 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):

$$FeCO_3 + 2Fe = 3FeO + C$$
 Eq. 2

$$FeCO_3 + 5Fe = 3FeO + Fe_3C$$
 Eq. 3

Fe₃C can also serve as a reduced C source to form diamonds through the following redox reaction (Bataleva *et al.*, 2016):

$$Fe_3C + 3Fe_2O_3 = 9FeO + C$$
 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:

$$Fe-C melt + Fe_2O_3 = 3FeO + C$$
 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 Fe₃C 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 Δ^{13} C between these phases,

$$\Delta^{13}C^{B-A} = 1000(\ln\beta_B - \ln\beta_A) \qquad \text{Eq. 6}$$

where A and B 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 MgCO₃, FeCO₃, Fe₃C and diamond (Tables S-1, S-2) at the P-T conditions of subducted slabs in the mantle. We also measured the PDOS of Fe²⁺ in FeCO₃ 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 Fe²⁺ in FeCO₃ 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 Fe₃C (Fig. S-1). Synchrotron Mössbauer spectra (Fig. S-2) and optical images (Fig. S-3) show that the spin transition of Fe²⁺ in FeCO₃ 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 \sim 5 % decrease of the β -factor of C in LS FeCO₃ compared to its HS state (Fig. S-5) as the C-O bound length is lengthened by 2.1 % (Fig. S-4). The magnetic state of Fe₃C 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 Fe₃C 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 $\Delta C^{\text{Dia-Fe}_3\text{C}}$ is larger than other inter-mineral fractionations involving diamond, such as $\Delta C^{\text{Dia-Carbonates}}$ (Fig. S-6). Our calculated $\Delta C^{\text{Dia-Fe}_3C}$ 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 $\Delta C^{\text{Dia-Fe}_3\text{C}}$ reported by Horita and Polyakov (2015). Therefore the 1-bar data would overestimate the C isotopic fractionation during diamond formation from a Fe₃C 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 δ^{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 δ^{13} C values.

The C isotopic fractionation can be modelled by using a Rayleigh distillation if the diamonds produced do not backreact 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, $\Delta^{13}C^{Dia-FeC melt}$ is calculated by the sum of $\Delta^{13}C^{\text{Dia-Fe}_3C}$ (Fig. S-6) and the equilibrium fractionation $\Delta^{13}C^{\text{Fe}_3\text{C-FeC melt}} = -5.6 \times 10^6/\text{T}^2$ 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 δ^{13} C values.





Figure 1 Partial phonon density of states (PDOS) of 57 Fe (**a**, **b**) and 12 C (**c**, **d**) in FeCO₃ at high pressures. In (**a**) and (**b**), the open cycles are PDOS of Fe measured by NRIXS; the blue curves are calculated PDOS of Fe by DFT + *U*. The red curves in (**c**) and (**d**) are calculated PDOS of C. The lowest energy peak at 20-40 meV can be attributed to the acoustic phonons. According to previous high pressure Raman and infrared studies of FeCO₃ (Santillán and Williams, 2004; Lin *et al.*, 2012), the other peaks can be assigned to librational mode (L), translational mode (T) and in-plane bending mode (v4), out of plane bending vibration (v2) and asymmetric stretch (v3) of CO₃²⁻ (marked as dashed vertical lines). The energies of v2 and v3 modes (marked as dotted vertical lines) at 60 GPa are linearly extrapolated from those measured up to 50 GPa for FeCO₃ (Santillán and Williams, 2004). In the PDOS of Fe at 60 GPa (**b**), the splitting of v4 mode at approximately 100-120 meV has also been observed in a previous Raman study (Lin *et al.*, 2012), which is explained as a result of the enhanced interaction between low-spin Fe²⁺ and neighbouring CO₃²⁻ units.

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*),

$$g(\delta^{13}C^{\text{Dia}}) = 1/\Delta^{13}C^{\text{Dia-Source}} \exp[(\delta^{13}C^{\text{Dia}} - \delta^{13}C_0^{\text{Source}})/\Delta^{13}C^{\text{Dia-Source}} - 1]$$
Eq. 7

The PDFs for $\Delta^{13}C^{\text{Dia-Fe}_3C}$ at representative upper mantle, transition zone, and lower mantle depths are shown in Figure 2. For each PDF, $\delta^{13}C_0^{\text{Source}}$ 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 $\Delta^{13}C^{\text{Dia-Fe}C}$ 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 β -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 δ^{13} C of super-deep diamonds from different carbon sources are derived. Based on the comparison between the histogram for δ^{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.





Figure 2 Comparison of the histogram for δ^{13} C of super-deep diamonds (left axis) and the probability density functions (PDFs, right axis) of δ^{13} C^{Dia} derived from metallic melt for different *P-T* conditions. The red, green and black solid curves are calculated PDFs by using Δ^{13} C^{Dia-FeC melt} at 250 km, 660 km and 1500 km depths along a cold slab geotherm (Yang *et al.*, 2017), respectively. The yellow dotted curve is calculated by using Δ^{13} C^{Dia-FeC melt} at 250 km along the modern mantle geotherm (Yang *et al.*, 2017), which may be similar to the Archean mantle geotherm (Santosh *et al.*, 2010). The pink dashed curve is for diamonds forming from C-H-O fluids, which is calculated using the largest reported value of Δ^{13} C^{Dia-COH} (-2.9 ‰) (Cartigny *et al.*, 2014). The inset figure shows the negative tailings of these three PDFs. δ^{13} C data of super-deep diamonds are from Cartigny *et al.* (2014).

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Author Contributions

J.C. Liu and W.Z. Wang contributed equally to this work. J.F. Lin, J.C. Liu and W.Z. Wang designed this project; J.C. Liu, H. Yang, N. Dauphas, M.Y. Hu, J.Y. Zhao, W.L. Bi, E.E. Alp, W. Liang and B. Chen performed the experiments and data analysis; W.Z. Wang and Z.Q. Wu performed the calculations; J.C. Liu, W.Z. Wang, N. Dauphas and J.F. Lin wrote the paper.

Additional Information

Supplementary Information accompanies this letter at http:// www.geochemicalperspectivesletters.org/article1915.



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Supplementary Information

The Supplementary Information includes:

- 1. High-Pressure Experiment
- ➢ 2. First-Principles Calculations
- > 3. C Isotope Model
- ➤ Tables S-1 and S-2
- ➢ Figures S-1 to S-9
- Supplementary Information References

1. High-Pressure Experiment

⁵⁷FeCO₃ Sample Synthesis

⁵⁷FeCO₃ single-crystal sample was synthesised through redox reaction between Fe₂O₃ and H₂C₂O₄ in a DS 6*600t cubic-anvil-type apparatus at 2.5 GPa and 973 K for 1 hour following the chemical reaction (Liang *et al.*, 2018):

 ${}^{57}Fe_2O_3 + 2H_2C_2O_4 = 2{}^{57}FeCO_3 + CO_2(g) + CO(g) + 2H_2O$

Through this redox reaction, Fe^{3+} in Fe_2O_3 is reduced by $H_2C_2O_4$ to form $FeCO_3$. Starting material was a mixture of 96.64 % ⁵⁷Feenriched Fe_2O_3 (Cambridge Isotope Laboratories) and anhydrous $H_2C_2O_4$ (98 %, Alfa Aesar) with a molar ratio of 1:2. The extra $H_2C_2O_4$ was used to maintain the oxygen fugacity to CO/CO_2 level and reduce residual stress during single-crystal nucleation and growth. The starting material was loaded into a platinum capsule (0.1 mm in thickness, 5 mm in diameter and 3 mm in length), which was surrounded by *h*-BN as pressure medium. The sample was heated by a graphite heater and temperature was monitored by K-type thermocouples. The sample assembly was first compressed to target pressure and then heated at 973 K for 1 hour before quenching. The composition and structure of our single-crystal ⁵⁷FeCO₃ were confirmed by electron microprobe, single-crystal Xray diffraction and Raman spectroscopy (Liang *et al.*, 2018).

High-Pressure Diamond Anvil Cells (DACs) Experiments

Three panoramic three-pin diamond anvil cells (DACs) with different types of diamonds and culet sizes were used to generate



pressures up to 61.7 GPa at 300 K. ⁵⁷FeCO₃ samples were double-polished to ~20 μ m thick and ~40 μ m*40 μ m in diameter. For nuclear resonance inelastic X-ray scattering (NRIXS) measurements at 12.1 GPa and 21.6 GPa, a DAC with a pair of 400- μ m culet diamonds was used, while the upstream diamond was perforated in order to reduce the scattering of income X-ray from the upstream diamond. For the same purpose, one 300- μ m mini anvil with a height of about 1 mm together with a normal downstream 300- μ m anvil were used for the measurements between 32.0 and 52.5 GPa. The third DAC with a pair of 200- μ m diamonds was employed for the measurement at 61.7 GPa. X-ray transparent and high-purity Be gaskets of 3 mm in diameter with cubic boron nitride (c-BN) insert served as sample chamber, which were preindented to ~ 30 μ m thick with a hole of ~70 μ m in diameter. The pressure medium was mineral oil (Alfa Aesar, 31911) and 5- μ m ruby spheres next to the samples were used as pressure gauge. Pressure uncertainty was determined by the pressure shift before and after each NRIXS measurement (Mao *et al.*, 1986). In addition, 1-bar NRIXS measurement was collected from a piece of siderite sample mounted on top of a thin stick.

NRIXS and Synchrotron Mössbauer Spectroscopy (SMS) Measurements and Data Analysis

Both NRIXS and SMS measurements on ⁵⁷FeCO₃ were performed at sector 3ID-B of the Advanced Photon Source, Argonne National Laboratory. A monochromatic X-ray beam of ~ 14.4125 keV with 24 bunches separated by 153.4 ns was used to excite the nuclear resonance of the ⁵⁷Fe nuclei in FeCO₃ sample. The NRIXS signals were collected by two avalanche photodiode detectors (APDs) on the side windows of the panoramic cells and a third one in the forward direction. As noticed by recent NRIXS studies (Dauphas *et al.*, 2012, 2014; Liu *et al.*, 2017; Shahar *et al.*, 2016), background removal is critical for deriving robust force constant, which requires long range of energy scan. Therefore, the energy range in our experiments was -160 meV to +170 meV around the nuclear resonance energy of ⁵⁷Fe for 1-bar measurement and -120 meV to +130 meV for high pressure ones. The energy resolution was 1 meV with a step size of 0.334 meV and a collection time of 3 s/step. Below the pressures of spin transition of Fe²⁺, 7-12 scans were enough to accumulate 200-350 counts in the strongest inelastic peak. But the inelastic peaks collapsed across the spin transition of Fe²⁺ (Fig. S-8), therefore 14-20 scans were required to achieve good statistics. The complementary synchrotron Mössbauer spectroscopy (SMS) data were collected by the APD in the forward direction (Fig. S-2).

2. First-Principles Calculations

We calculated the vibrational phonon density of state (PDOS) of C in FeCO₃, MgCO₃, CaCO₃, Fe₃C, diamond and the PDOS of Fe in FeCO₃ and Fe₃C by an open-source software "Quantum Espresso". It bases on the density functional theory (DFT), plane wave, and pseudopotential (Giannozzi *et al.*, 2009). The calculation details are similar to previous studies (Huang *et al.*, 2013, 2014; Feng *et al.*, 2014; Wu *et al.*, 2015; Wang *et al.*, 2017a,b). The pseudopotentials for C, Fe and Ca are generated using the Vanderbilt method (Vanderbilt, 1990) with the configuration of 2s²2p² and a cutoff radius of 1.3 Bohr for C, the configuration of 3s²3p⁶3d^{6.5}4s¹4p⁰ and a cutoff radius of 1.8 Bohr for Fe, and the configuration 3s²3p⁶4s¹ and a cutoff radius of 1.85 Bohr for Ca. The pseudopotential for Mg is generated using the method of von Barth and Car for all channels using a cutoff radius of 2.5 Bohr and five configurations, 3s²3p⁰, 3s¹3p¹, 3s¹3p^{0.5}3d^{0.5}, 3s¹3d¹, with weights of 1.5, 0.6, 0.3, 0.3, 0.2, respectively. The pseudopotentials for oxygen is generated using the method of Troullier and Martins (1991) with the configuration 2s²2p⁴ and a cutoff radius of 1.45 Bohr.

All crystal structures are well optimised at various pressures using the method of variable cell shape molecular dynamics (Wentzcovitch, 1991). For FeCO₃, MgCO₃, CaCO₃, Fe₃C and diamond, the electronic states are sampled on a shifted 8×8×8, 8×8×8, 8×8×8, 6×6×6 and 10×10×10, respectively. The plane-wave cutoff energy is 70 Ry and the residual forces converge within 10⁴ Ry/Bohr. For MgCO₃, CaCO₃ and diamond, here we adopt the local density approximation (LDA) (Perdew and Zunger, 1981) for exchange correlation functional due to its advantages on calculating structures and thermodynamic properties of minerals (Wentzcovitch *et al.*, 2010; Huang *et al.*, 2013). For Fe-bearing phases, we introduced a Hubbard *U* correction to the LDA (LDA+*U*) to sufficiently treat the large on-site Coulomb interactions among Fe 3d electrons. The Hubbard *U* values were non-empirically calculated using linear response method (Cococcioni and de Gironcoli, 2005) at different pressures. The calculated compression curve and the pressure dependence of Fe-O and C-O bonds match well with previous experimental study (Fig. S-4)

After performing optimisations for all crystal structures, we calculated their phonon frequencies and PDOS using the ab initio lattice dynamics (LD) (Alfè, 2009) method. Mass-dependent equilibrium isotope fractionation factors can be calculated from the changes in vibrational frequencies caused by isotopic substitution of an element in two phases (Bigeleisen and Mayer, 1947; Urey, 1947). Following Richet *et al.* (1977), the reduced partition function ratio β_A of an element X in phase A, which also represents the equilibrium isotope fractionation factor between phase A and atomic X vapor, can be obtained within the harmonic approximation from:



Letter

$$\mathcal{D}_{A} = \frac{Q_{h}}{Q_{l}} = \prod_{i}^{3N} \frac{u_{ih}}{u_{il}} \frac{e^{-\frac{1}{2}u_{ih}}}{1 - e^{-u_{ih}}} \frac{e^{-\frac{1}{2}u_{il}}}{1 - e^{-u_{il}}}$$
Eq. S-1

In this equation, Q_h and Q_l are the vibrational partition functions in which h and l correspond to the heavy and light isotopes, respectively; i is the running index of vibrational frequency mode and N is the number of atoms. u_{il} or u_{il} is defined as:

$$u_{ihoril} = h w_{ihoril} / k_B T$$
 Eq. S-2

where *h* and *k*^B refer to the Planck and Boltzmann constant, respectively; *T* is temperature in Kelvin, and ω_{ihoril} is the vibrational frequency of the *i*th mode. Based on the comparison of calculated and measured vibrational frequencies of carbonates (Wang *et al.*, 2017a), the relative uncertainties of calculated 10³ln β and Δ^{13} C are 4 % and 6 %, respectively. These relative uncertainties result in 5-6 % relative uncertainty in both calculated δ^{13} C^{Dia} through Rayleigh distillation and the corresponding PDFs (Fig. 2).

3. C Isotope Model

Rayleigh Distillation Model

 δ^{13} C of diamonds formed from either oxidised (carbonates) or reduced (carbide) source is calculated by a Rayleigh distillation model. With the remaining fraction of carbon in carbonates or carbide as f_{C}^{Source} , $\delta^{13}C^{Source}$ of the residual source is expressed as follows:

$$\delta^{13}C^{\text{Source}} = \delta^{13}C_0^{\text{Source}} + \Delta^{13}C^{\text{Dia-Source}} \cdot lnf_C^{\text{Source}}$$
 Eq. S-3

Here $\delta^{13}C_0^{\text{Source}}$ is the initial C isotopic composition of depositional carbonates (~0 ‰, Krissansen-Totton *et al.*, 2015) or carbide (~-10 ‰, Horita and Polyakov, 2015); $\Delta^{13}C^{\text{Dia-Source}}$ is the equilibrium isotopic fractionation between diamond and carbonates/carbide.

Based on a conservation of bulk isotopic composition, the accumulated $\delta^{13}C^{Dia}$ of crystallised diamonds is calculated using the following equation:

$$\delta^{13}C^{\text{Dia}} = \delta^{13}C_0^{\text{Source}} - \Delta^{13}C^{\text{Dia-Source}} \cdot f_C^{\text{Source}} \cdot lnf_C^{\text{Source}} / (1-f_C^{\text{Source}})$$
 Eq. S-4

By using Equation S-4, $\delta^{13}C^{Dia}$ forming from carbonates sources at depths are calculated (Fig. S-9). Given the averaged $\delta^{13}C$ of carbonates as 0 % (Krissansen-Totton *et al.*, 2015), reduction of carbonates can produce diamonds with $\delta^{13}C$ as low as -2.6 % (Fig. S-9). Spin transition of Fe²⁺ in carbonates only introduces up to 0.7 % increases in $\Delta^{13}C^{Dia-FeCO_3}$ (Fig. S-6), which results in up to +0.5% shift in $\delta^{13}C$ of diamonds forming from a carbonates source (Fig. S-9).

If crystallised diamonds separate from their source efficiently, possibly due to the high mobility of C source, $\delta^{13}C^{Dia}$ is calculated based on instantaneous equilibrium relationship:

$$\delta^{13}C^{\text{Dia}} = \delta^{13}C^{\text{Source}} + \Delta^{13}C^{\text{Dia-Source}}$$

$$= \delta^{13}C_0^{\text{Source}} + \Delta^{13}C^{\text{Dia-Source}} \cdot (1 + \ln f c^{\text{Source}}) \qquad \text{Eq. S-5}$$

C Isotopes of Super-deep Diamonds Formed from Metallic Melt

As a Rayleigh distillation proceeds, reactants are converted into products, which are removed from the system. The aim of the

Geochem. Persp. Let. (2019) 10, 51-55 | doi: 10.7185/geochemlet.1915



derivation below is to calculate what fraction of the products acquire a given isotopic composition. Statistically, this corresponds to the probability density function (PDF) of the $\delta^{13}C^{Dia}$ values of the instantaneous diamond forming from metallic liquid.

Equation S-5 can be rewritten to express $f_{C^{\text{Source}}}$ as a function of $\delta^{13}C^{\text{Dia}}$,

$$f_{\rm C}^{\rm Source} = \exp[(\delta^{13}{\rm C}^{\rm Dia} - \delta^{13}{\rm C}_0^{\rm Source})/\Delta^{13}{\rm C}^{\rm Dia-Source} -1]$$
 Eq. S-6

The corresponding fraction (*p*) of diamond can be expressed as below:

$$p = 1 - f_{C}^{Source}$$

= 1- exp[($\delta^{13}C^{Dia} - \delta^{13}C_{0}^{Source}$)/ $\Delta^{13}C^{Dia-Source}$ -1] Eq. S-7

If we take $\Delta^{13}C^{\text{Dia-Source}}$ positive, $\delta^{13}C^{\text{Dia-starts}}$ at ($\delta^{13}C^{\text{Source}} + \Delta^{13}C^{\text{Dia-Source}}$) at the onset of the reaction and finishes at - ∞ when the source is exhausted. The PDF of $\delta^{13}C^{\text{Dia}}$, which we note $g(\delta^{13}C^{\text{Dia}})$, corresponds to the fraction of diamonds removed dp with isotopic composition between $\delta^{13}C^{Dia}$ and $\delta^{13}C^{Dia}$, is simply given by (the negative sign is because for positive $\Delta^{13}C^{Dia-Source}$, $\delta^{13}C^{Dia}$) decreases when *p* increases),

$$g(\delta^{13}C^{\text{Dia}}) = -dp / d\delta^{13}C^{\text{Dia}}$$
$$= 1/\Delta^{13}C^{\text{Dia-Source}} \cdot \exp[(\delta^{13}C^{\text{Dia}} - \delta^{13}C_0^{\text{Source}}) / \Delta^{13}C^{\text{Dia-Source}} - 1] \qquad \text{Eq.}$$

We can check that this indeed corresponds to a PDF by calculating the integral,

$$\int_{-\infty}^{\Delta+\delta^{13}C_0^{\text{Source}}} g(\delta^{13}C^{\text{Dia}}) \, d\delta^{13}C^{\text{Dia}} = 1$$
 Eq. S-9

The corresponding cumulative distribution function (CDF) is:

$$CDF (\delta^{13}C^{\text{Dia}}) = \exp[(\delta^{13}C^{\text{Dia}} - \delta^{13}C_0^{\text{Source}}) / \Delta^{13}C^{\text{Dia-Source}} - 1]$$
Eq. S-10

The PDF can also be calculated when Δ^{13} CDia-Source < 0 but in this case, takes its values between $\delta_0 + \Delta$ and $+\infty$, and the sign of Equation S-8 changes. A general formula that is applicable to both positive and negative values of Δ is therefore,

$$g(\delta^{13}C^{\text{Dia}}) = 1/|\Delta^{13}C^{\text{Dia-Source}}| \cdot \exp[(\delta^{13}C^{\text{Dia}} - \delta^{13}C_0^{\text{Source}})/\Delta^{13}C^{\text{Dia-Source}} - 1]$$
 Eq. S-11

$$CDF (\delta^{13}C^{\text{Dia}}) = \exp[(\delta^{13}C^{\text{Dia}} - \delta^{13}C_0^{\text{Source}}) / |\Delta^{13}C^{\text{Dia-Source}}| -1]$$
Eq. S-12

Eq. S-8

200 6.5 1672 8.9 8.8 - 2.1 7.2 1724 15.2 15.1 - 3.8 12.4 216 7.0 1677 8.8 8.8 - 2.1 7.2 1274 15.2 15.1 15.0 - 3.8 12.4 246 8.0 1683 8.8 8.7 - 2.1 7.1 1291 14.9 14.8 - 3.7 12.0 275 9.0 1701 8.6 8.5 - 2.1 7.0 1301 14.7 14.4 14.3 - 3.6 11.7 303 10.0 1722 8.5 8.5 - 2.1 6.9 1328 14.2 14.4 14.0 - 3.6 11.7 310 172 8.5 8.5 - 2.1 6.8 1340 14.1 14.0 - 3.6 11.3 313 11.2 8.5 8.5 -	Depth (km)	P (GPa)	Mantle T (K)	MgCO ₃	HS FeCO ₃	LS FeCO ₃	Fe ₃ C	Dia	Slab T (K)	MgCO ₃	HS FeCO ₃	LS FeCO ₃	Fe ₃ C	Dia
121 7.0 1674 8.9 8.8 21.1 7.2 1274 15.2 15.1 3.8 124 246 8.0 1683 8.8 8.7 21.1 7.1 1283 15.0 14.9 3.8 124 260 8.5 1691 8.7 8.7 21.1 7.1 1201 14.9 14.8 3.6 117 287 9.0 1701 8.6 8.5 21.1 6.9 1322 14.3 14.2 3.6 11.6 303 10.0 1726 8.5 8.4 21.1 6.9 1322 14.3 14.2 3.6 11.7 310 1722 8.5 8.4 21.6 6.9 1322 14.3 14.3 14.3 14.3 14.3 14.3 14.3 14.3 14.3 14.3 14.3 14.3 14.3 </td <td>200</td> <td>6.5</td> <td>1672</td> <td>8.9</td> <td>8.8</td> <td>-</td> <td>2.1</td> <td>7.2</td> <td>1272</td> <td>15.2</td> <td>15.1</td> <td>-</td> <td>3.8</td> <td>12.4</td>	200	6.5	1672	8.9	8.8	-	2.1	7.2	1272	15.2	15.1	-	3.8	12.4
231 7.5 1677 8.8 8.8 - 2.1 7.2 1277 15.1 15.0 - 3.8 12.3 246 8.5 1691 8.7 8.7 - 2.1 7.1 1291 14.9 14.8 - 3.7 12.0 289 9.5 1710 8.6 8.5 - 2.1 7.0 1310 14.5 14.4 - 3.6 11.9 303 10.0 1722 8.5 8.5 - 2.1 6.9 1328 1.4.1 1.4.0 - 3.6 11.5 304 11.0 1728 8.5 8.4 - 2.1 6.8 1340 14.0 13.9 - 3.5 11.4 303 12.5 1746 8.3 8.3 - 2.0 6.7 1388 13.7 1.3.5 11.3 341 11.3 13.0 175 8.1 8.1 - 2.0 6.7 </td <td>216</td> <td>7.0</td> <td>1674</td> <td>8.9</td> <td>8.8</td> <td>-</td> <td>2.1</td> <td>7.2</td> <td>1274</td> <td>15.2</td> <td>15.1</td> <td>-</td> <td>3.8</td> <td>12.4</td>	216	7.0	1674	8.9	8.8	-	2.1	7.2	1274	15.2	15.1	-	3.8	12.4
246 8.0 1683 8.8 8.7 7. 2.1 7.1 1283 15.0 14.9 - 3.8 12.3 250 8.5 1691 8.7 8.7 - 2.1 7.0 1301 14.5 14.4 - 3.7 12.2 259 9.5 1710 8.6 8.5 - 2.1 6.9 1316 14.4 14.3 - 3.6 11.7 332 11.0 1728 8.5 8.4 - 2.1 6.8 1334 14.1 14.0 - 3.6 11.7 332 11.0 1728 8.3 8.3 - 2.0 6.8 1340 14.0 13.9 3 11.1 340 1272 8.4 8.3 - 2.0 6.7 1388 13.8 1.8 1.1 13.3 13.7 13.6 3 3.5 11.2 414 140 176 8.3 8.2<	231	7.5	1677	8.8	8.8	-	2.1	7.2	1277	15.1	15.0	-	3.8	12.4
260 8.5 1691 8.7 8.7 - 2.1 7.1 1291 14.9 14.8 - 3.7 122 289 9.5 1700 8.6 8.5 - 2.1 7.0 1301 14.5 14.4 - 3.6 11.8 303 10.0 1716 8.5 8.5 - 2.1 6.9 1322 14.3 14.2 - 3.6 11.8 318 10.5 1722 8.5 8.4 - 2.1 6.8 1340 14.1 14.0 - 3.6 11.4 346 11.5 1734 8.4 8.4 - 2.1 6.8 1340 14.0 13.9 - 3.5 11.4 373 12.5 1746 8.4 8.3 - 2.0 6.7 1388 13.7 13.6 35 11.2 414 14.0 1763 8.1 8.1 - 2.0 6.6 <td>246</td> <td>8.0</td> <td>1683</td> <td>8.8</td> <td>8.7</td> <td>-</td> <td>2.1</td> <td>7.1</td> <td>1283</td> <td>15.0</td> <td>14.9</td> <td>-</td> <td>3.8</td> <td>12.3</td>	246	8.0	1683	8.8	8.7	-	2.1	7.1	1283	15.0	14.9	-	3.8	12.3
1275 9.0 1701 8.6 8.6 - 2.1 7.0 1301 14.7 14.4 - 3.6 11.9 303 10.0 1716 8.5 8.5 - 2.1 6.9 1306 14.4 14.3 - 3.6 11.8 318 10.5 1722 8.5 8.5 - 2.1 6.9 1328 14.2 14.1 - 3.6 11.6 336 11.0 1728 8.5 8.4 - 2.1 6.8 1340 14.0 13.9 3 5.1 1.5 337 12.5 1746 8.3 8.3 - 2.0 6.7 1388 13.8 1.3 .3 1.1 .3 1.1 .3 1.1 .3 1.1 .3 .3 1.1 414 14.0 1769 8.2 8.1 - 2.0 6.6 1369 13.5 1.3 .3 .3 .11.1	260	8.5	1691	8.7	8.7	-	2.1	7.1	1291	14.9	14.8	-	3.7	12.2
289 9.5 1710 8.6 8.5 - 2.1 7.0 1310 14.5 14.4 - 3.6 11.8 303 100.0 1716 8.5 8.5 - 2.1 6.9 1322 14.3 14.2 - 3.6 11.7 332 11.0 1728 8.5 8.4 - 2.1 6.8 1334 14.1 14.0 - 3.6 11.5 346 11.5 1734 8.4 8.4 - 2.1 6.8 1334 14.1 14.0 - 3.6 11.5 373 12.5 1746 8.3 8.3 - 2.0 6.7 1338 13.7 13.7 3 5 11.2 481 1706 8.2 8.1 - 2.0 6.6 1381 13.4 13.3 - 3.4 11.0 441 16.0 1786 8.1 8.0 - 2.0 6.5	275	9.0	1701	8.6	8.6	-	2.1	7.0	1301	14.7	14.6	-	3.7	12.0
	289	9.5	1710	8.6	8.5	-	2.1	7.0	1310	14.5	14.4	-	3.6	11.9
318 10.5 1722 8.5 8.5 - 2.1 6.9 1322 14.3 14.2 - 3.6 11.6 346 11.5 1734 8.4 8.4 - 2.1 6.8 1334 14.1 14.0 - 3.6 11.5 370 12.2 1740 8.4 8.3 - 2.0 6.8 1344 14.0 1.9 - 3.5 11.1 373 12.5 1736 8.3 8.3 - 2.0 6.7 1358 1.3 1.3 .7 3.5 11.1 414 14.0 1763 8.2 8.2 2.0 6.6 1357 13.6 .3 3.4 11.1 428 14.5 1757 8.1 8.1 - 2.0 6.6 1375 13.3 1.3 .3 .3 1.4 1.4 1.0 441 15.0 1757 8.1 8.0 - 2.0	303	10.0	1716	8.5	8.5	-	2.1	6.9	1316	14.4	14.3	-	3.6	11.8
332 11.0 1728 8.5 8.4 - 2.1 6.9 1328 14.2 14.1 - 3.6 11.5 346 11.5 1744 8.4 8.3 - 2.1 6.8 1340 14.0 13.9 - 3.5 11.5 373 12.5 1746 8.3 8.3 - 2.0 6.7 1352 13.8 13.8 13.8 13.7 - 3.5 11.1 401 13.5 1788 8.2 8.2 - 2.0 6.67 1363 13.7 13.6 - 3.5 11.2 428 14.5 1769 8.2 8.1 - 2.0 6.6 1367 13.5 13.4 - 3.4 11.0 455 155 1781 8.1 8.0 - 2.0 6.5 1392 13.2 13.2 - 3.4 10.8 455 15.0 1781 8.0 8.0	318	10.5	1722	8.5	8.5	-	2.1	6.9	1322	14.3	14.2	-	3.6	11.7
346 1.15 1.734 8.4 8.4 - 2.1 6.8 1334 1.4.1 1.4.0 - 3.5 11.5 373 12.5 1746 8.3 8.3 - 2.0 6.8 1346 13.9 13.9 - 3.5 11.1 373 13.0 1752 8.3 8.3 - 2.0 6.7 1358 13.7 13.6 - 3.5 11.2 414 14.0 1763 8.2 8.1 - 2.0 6.6 1369 13.6 13.5 3 3.4 11.1 428 16.0 1765 8.1 8.1 - 2.0 6.6 1375 13.3 13.3 - 3.4 11.0 458 16.0 1786 8.1 8.0 - 2.0 6.5 1386 13.3 13.2 3 3.4 10.9 481 16.5 1792 8.0 8.0 -	332	11.0	1728	8.5	8.4	-	2.1	6.9	1328	14.2	14.1	-	3.6	11.6
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373 12.5 1746 8.3 8.3 - 2.0 6.8 1346 13.9 13.9 - 3.5 11.3 387 13.0 1752 8.3 8.2 - 2.0 6.7 1338 13.7 13.7 - 3.5 11.2 414 14.0 1763 8.2 8.2 - 2.0 6.6 1363 13.7 13.5 - 3.4 11.1 441 15.0 1775 8.1 8.1 - 2.0 6.6 1375 13.5 13.4 13.4 - 3.4 11.0 455 15.5 1781 8.1 8.0 - 2.0 6.5 1386 13.3 13.2 - 3.4 10.8 456 16.0 1786 8.1 8.0 8.0 - 2.0 6.5 1386 13.1 13.1 - 3.3 10.6 533 18.0 18.09 7.9 7.9 - 2.0 6.4 1420 12.8 - 3.3 10.6 <	360	12.0	1740	8.4	8.3	-	2.1	6.8	1340	14.0	13.9	-	3.5	11.5
387 13.0 1752 8.3 8.3 - 2.0 6.7 1352 13.8 13.8 - 3.5 11.2 414 14.0 1763 8.2 8.2 - 2.0 6.7 1363 13.7 13.6 - 3.5 11.2 428 14.5 1769 8.2 8.1 - 2.0 6.6 1369 13.6 1.35 - 3.4 11.1 455 15.5 1781 8.1 8.1 - 2.0 6.6 1381 1.34 1.33 - 3.4 10.9 468 16.0 1786 8.0 8.0 - 2.0 6.5 1398 13.2 13.1 - 3.4 10.8 507 17.5 1803 8.0 7.9 - 2.0 6.4 1409 13.0 12.9 - 3.3 10.6 533 18.5 1814 7.9 7.9 - 2.0 <td>373</td> <td>12.5</td> <td>1746</td> <td>8.3</td> <td>8.3</td> <td>-</td> <td>2.0</td> <td>6.8</td> <td>1346</td> <td>13.9</td> <td>13.9</td> <td>-</td> <td>3.5</td> <td>11.4</td>	373	12.5	1746	8.3	8.3	-	2.0	6.8	1346	13.9	13.9	-	3.5	11.4
401 135 1788 8.3 8.2 - 2.0 6.7 1388 13.7 13.7 - 3.5 11.2 414 14.0 1763 8.2 8.2 - 2.0 6.6 1369 13.6 13.5 - 3.5 11.2 441 15.0 1775 8.1 8.1 - 2.0 6.6 1381 13.4 13.3 - 3.4 11.0 455 15.5 1781 8.1 8.0 - 2.0 6.5 1386 13.3 13.2 - 3.4 10.8 481 16.5 1792 8.0 8.0 - 2.0 6.5 1398 13.2 13.1 - 3.4 10.8 507 17.5 1803 8.0 7.9 - 2.0 6.4 1403 13.1 1.3 - 3.3 10.6 533 18.5 1814 7.9 7.9 - 2.0	387	13.0	1752	8.3	8.3	-	2.0	6.7	1352	13.8	13.8	-	3.5	11.3
	401	13.5	1758	8.3	8.2	-	2.0	6.7	1358	13.7	13.7	-	3.5	11.2
42814517698.28.1-2.06.6136913.613.5-3.411.144115.517758.18.1-2.06.6137513.4-3.411.045515.517818.18.1-2.06.5138613.313.2-3.410.948116.517928.08.0-2.06.5139813.213.2-3.410.850717.518038.07.9-2.06.5140313.113.0-3.310.652018.018097.97.9-2.06.4140913.012.9-3.310.655919.518207.97.8-2.06.4142012.812.8-3.310.45712.0018317.87.8-2.06.4142012.812.7-3.310.45842.0518367.87.7-2.06.3143112.712.6-3.310.359621.018427.77.7-2.06.3143412.612.4-3.210.261422.018527.77.6-1.96.2145212.4-3.210.261422.018637.67.6-1.96.2	414	14.0	1763	8.2	8.2	-	2.0	6.7	1363	13.7	13.6	-	3.5	11.2
	428	14.5	1769	8.2	8.1	-	2.0	6.6	1369	13.6	13.5	-	3.4	11.1
$ \begin{array}{ c c c c c c c c c c c c c c c c c c c$	441	15.0	1775	8.1	8.1	-	2.0	6.6	1375	13.5	13.4	-	3.4	11.0
$ \begin{array}{ c c c c c c c c c c c c c c c c c c c$	455	15.5	1781	8.1	8.1	-	2.0	6.6	1381	13.4	13.3	-	3.4	11.0
48116.517928.08.0-2.06.5139213.213.2-3.410.849417.0177518038.08.0-2.06.5139813.113.1-3.410.850717.518038.07.97.9-2.06.4140913.012.9-3.310.653318.518147.97.9-2.06.4141412.812.8-3.310.653319.018207.97.8-2.06.4142512.812.8-3.310.655919.518257.87.8-2.06.3143112.712.6-3.310.457120.018317.87.8-2.06.3143212.612.6-3.310.359621.018427.77.7-2.06.3144212.612.4-3.210.263422.518567.67.6-1.96.2145212.412.4-3.210.263422.518687.67.6-1.96.2145812.312.2-3.210.164623.018637.67.5-1.96.1147312.112.1-3.210.065823.51868<	468	16.0	1786	8.1	8.0	-	2.0	6.5	1386	13.3	13.2	-	3.4	10.9
$ \begin{array}{ c c c c c c c c c c c c c c c c c c c$	481	16.5	1792	8.0	8.0	-	2.0	6.5	1392	13.2	13.2	-	3.4	10.8
$ \begin{array}{ c c c c c c c c c c c c c c c c c c c$	494	17.0	1798	8.0	8.0	-	2.0	6.5	1398	13.2	13.1	-	3.4	10.8
$ \begin{array}{ c c c c c c c c c c c c c c c c c c c$	507	17.5	1803	8.0	7.9	-	2.0	6.5	1403	13.1	13.0	-	3.3	10.7
53318.518147.97.97.9-2.06.4141412.912.83.310.654619.018207.97.8-2.06.4142012.812.83.310.555919.518257.87.8-2.06.4142112.812.73.310.457120018317.87.872.06.3143512.612.63.310.358420.518367.87.77.7.2.06.3144212.612.63.310.359621.018427.77.7.2.06.3144712.512.43.210.262122.018527.77.6.1.96.2145812.312.33.210.164423.018637.67.6.1.96.2145812.312.23.210.164623.018637.67.6.1.96.2146312.312.23.210.067024.018737.67.5.1.96.1147312.112.03.210.068224.518767.57.5.1.96.11478	520	18.0	1809	7.9	7.9	-	2.0	6.4	1409	13.0	12.9	-	3.3	10.6
54619.01820 7.9 7.8 $ 2.0$ 6.4 1420 12.8 12.8 12.8 $ 3.3$ 10.5 559 19.51825 7.8 7.8 $ 2.0$ 6.4 1425 12.8 12.7 $ 3.3$ 10.4 571 20.01831 7.8 7.8 $ 2.0$ 6.3 1431 12.7 12.6 $ 3.3$ 10.3 596 21.01842 7.7 7.7 $ 2.0$ 6.3 1442 12.6 12.6 $ 3.3$ 10.3 609 21.51847 7.7 7.7 $ 1.9$ 6.3 1447 12.5 12.4 $ 3.2$ 10.2 621 22.01852 7.7 7.6 $ 1.9$ 6.2 1452 12.4 12.4 $ 3.2$ 10.2 642 23.01863 7.6 7.6 $ 1.9$ 6.2 1463 12.3 12.3 $ 3.2$ 10.1 642 23.01863 7.6 7.6 $ 1.9$ 6.2 1468 12.2 12.2 $ 3.2$ 10.0 670 24.01873 7.6 7.5 $ 1.9$ 6.1 1473 12.1 12.1 $ 3.2$ 10.0 670 24.01873 7.6 7.5 $ 1.9$ 6.1 1473 12.1 12.0 $ 3.2$ 9.9 <td>533</td> <td>18.5</td> <td>1814</td> <td>7.9</td> <td>7.9</td> <td>-</td> <td>2.0</td> <td>6.4</td> <td>1414</td> <td>12.9</td> <td>12.8</td> <td>-</td> <td>3.3</td> <td>10.6</td>	533	18.5	1814	7.9	7.9	-	2.0	6.4	1414	12.9	12.8	-	3.3	10.6
559 19.5 1825 7.8 7.8 7.8 $ 2.0$ 6.4 1425 12.8 12.7 $ 3.3$ 10.4 571 20.0 1831 7.8 7.8 7.7 $ 2.0$ 6.3 1431 12.7 12.6 $ 3.3$ 10.3 584 20.5 1836 7.8 7.7 $ 2.0$ 6.3 1442 12.6 12.6 $ 3.3$ 10.3 609 21.5 1847 7.7 7.7 $ 1.9$ 6.3 1447 12.5 12.4 $ 3.2$ 10.2 621 22.0 1852 7.7 7.6 $ 1.9$ 6.2 1452 12.4 12.4 $ 3.2$ 10.1 634 22.5 1858 7.6 7.6 $ 1.9$ 6.2 1458 12.3 12.2 $ 3.2$ 10.1 634 23.5 1868 7.6 7.6 $ 1.9$ 6.2 1468 12.2 12.2 $ 3.2$ 10.1 658 23.5 1868 7.6 7.6 $ 1.9$ 6.1 1473 12.1 12.0 $ 3.2$ 10.0 682 24.5 1878 7.5 7.5 $ 1.9$ 6.1 1473 12.1 12.0 $ 3.2$ 9.9 705 25.5 1884 7.5 7.5 $ 1.9$ 6.1 1484 12.0 <	546	19.0	1820	7.9	7.8	-	2.0	6.4	1420	12.8	12.8	-	3.3	10.5
$ \begin{array}{ c c c c c c c c c c c c c c c c c c c$	559	19.5	1825	7.8	7.8	-	2.0	6.4	1425	12.8	12.7	-	3.3	10.4
584 20.5 1836 7.8 7.7 $ 2.0$ 6.3 1436 12.6 12.6 $ 3.3$ 10.3 596 21.0 1842 7.7 7.7 $ 2.0$ 6.3 1442 12.6 12.5 $ 3.3$ 10.3 609 21.5 1847 7.7 7.7 $ 1.9$ 6.3 1447 12.5 12.4 $ 3.2$ 10.2 621 22.0 1852 7.7 7.6 $ 1.9$ 6.2 1458 12.3 12.3 $ 3.2$ 10.1 646 23.0 1863 7.6 7.6 $ 1.9$ 6.2 1463 12.3 12.2 $ 3.2$ 10.1 646 23.0 1863 7.6 7.6 $ 1.9$ 6.2 1463 12.3 12.2 $ 3.2$ 10.0 642 24.0 1873 7.6 7.5 $ 1.9$ 6.1 1473 12.1 12.1 $ 3.2$ 10.0 682 24.5 1878 7.5 7.5 $ 1.9$ 6.1 1478 12.1 12.0 $ 3.2$ 9.9 705 25.5 1888 7.5 7.4 $ 1.9$ 6.1 1478 12.1 12.0 $ 3.2$ 9.9 705 25.5 1888 7.5 7.4 $ 1.9$ 6.1 1478 12.1 12.0 $-$ <td< td=""><td>571</td><td>20.0</td><td>1831</td><td>7.8</td><td>7.8</td><td>-</td><td>2.0</td><td>6.3</td><td>1431</td><td>12.7</td><td>12.6</td><td>-</td><td>3.3</td><td>10.4</td></td<>	571	20.0	1831	7.8	7.8	-	2.0	6.3	1431	12.7	12.6	-	3.3	10.4
$ \begin{array}{ c c c c c c c c c c c c c c c c c c c$	584	20.5	1836	7.8	7.7	-	2.0	6.3	1436	12.6	12.6	-	3.3	10.3
	596	21.0	1842	7.7	7.7	-	2.0	6.3	1442	12.6	12.5	-	3.3	10.3
	609	21.5	1847	7.7	7.7	-	1.9	6.3	1447	12.5	12.4	-	3.2	10.2
	621	22.0	1852	7.7	7.6	-	1.9	6.2	1452	12.4	12.4	-	3.2	10.2
646 23.0 1863 7.6 7.6 $ 1.9$ 6.2 1463 12.3 12.2 $ 3.2$ 10.1 658 23.5 1868 7.6 7.6 $ 1.9$ 6.2 1468 12.2 12.2 $ 3.2$ 10.0 670 24.0 1873 7.6 7.5 $ 1.9$ 6.1 1473 12.1 12.1 $ 3.2$ 10.0 682 24.5 1878 7.5 7.5 $ 1.9$ 6.1 1473 12.1 12.0 $ 3.2$ 9.9 694 25.0 1884 7.5 7.5 $ 1.9$ 6.1 1478 12.1 12.0 $ 3.2$ 9.9 705 25.5 1888 7.5 7.4 $ 1.9$ 6.1 1484 12.0 11.9 $ 3.1$ 9.8 716 26.0 1892 7.5 7.4 $ 1.9$ 6.1 1492 11.9 11.8 $ 3.1$ 9.8 728 26.5 1896 7.4 7.4 $ 1.9$ 6.0 1499 11.8 11.8 $ 3.1$ 9.8 739 27.0 1899 7.4 7.4 $ 1.9$ 6.0 1503 11.8 11.8 $ 3.1$ 9.7 751 27.5 1903 7.4 7.4 $ 1.9$ 6.0 1507 11.8 11.7 $ 3.$	634	22.5	1858	7.6	7.6	-	1.9	6.2	1458	12.3	12.3	-	3.2	10.1
658 23.5 1868 7.6 7.6 7.6 7.6 7.6 7.5 $ 1.9$ 6.2 1468 12.2 12.2 $ 3.2$ 10.0 670 24.0 1873 7.6 7.5 $ 1.9$ 6.1 1473 12.1 12.1 $ 3.2$ 10.0 682 24.5 1878 7.5 7.5 $ 1.9$ 6.1 1478 12.1 12.0 $ 3.2$ 9.9 694 25.0 1884 7.5 7.5 $ 1.9$ 6.1 1484 12.0 11.0 $ 3.2$ 9.9 705 25.5 1888 7.5 7.4 $ 1.9$ 6.1 1488 12.0 11.9 $ 3.1$ 9.8 716 26.0 1892 7.5 7.4 $ 1.9$ 6.1 1492 11.9 11.9 $ 3.1$ 9.8 728 26.5 1896 7.4 7.4 $ 1.9$ 6.0 1499 11.8 11.8 $ 3.1$ 9.8 739 27.0 1899 7.4 7.4 $ 1.9$ 6.0 1503 11.8 11.8 $ 3.1$ 9.7 751 27.5 1903 7.4 7.4 $ 1.9$ 6.0 1503 11.8 11.7 $ 3.1$ 9.7 773 28.5 1910 7.4 7.3 $ 1.9$ 6.0 1510	646	23.0	1863	7.6	7.6	-	1.9	6.2	1463	12.3	12.2	-	3.2	10.1
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	658	23.5	1868	7.6	7.6	-	1.9	6.2	1468	12.2	12.2	-	3.2	10.0
$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$	670	24.0	1873	7.6	7.5	-	1.9	6.1	1473	12.1	12.1	-	3.2	10.0
	682	24.5	1878	7.5	7.5	-	1.9	6.1	1478	12.1	12.0	-	3.2	9.9
$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$	694	25.0	1884	7.5	7.5	-	1.9	6.1	1484	12.0	12.0	-	3.2	9.9
$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$	705	25.5	1888	7.5	7.4	-	1.9	6.1	1488	12.0	11.9	-	3.1	9.8
$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$	716	26.0	1892	7.5	7.4	-	1.9	6.1	1492	11.9	11.9	-	3.1	9.8
$ \begin{array}{ c c c c c c c c c c c c c c c c c c c$	728	26.5	1896	7.4	7.4	-	1.9	6.1	1496	11.9	11.8	-	3.1	9.8
$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$	739	27.0	1899	7.4	7.4	-	1.9	6.0	1499	11.8	11.8	-	3.1	9.7
$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$	751	27.5	1903	7.4	7.4	-	1.9	6.0	1503	11.8	11.8	-	3.1	9.7
$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$	762	28.0	1907	7.4	7.4	-	1.9	6.0	1507	11.8	11.7	-	3.1	9.7
78429.019147.47.3-1.96.0151411.711.6-3.19.679529.519187.37.3-1.96.0151811.711.6-3.19.680630.019217.37.3-1.96.0152111.611.6-3.19.681730.519257.37.3-1.96.0152511.611.5-3.19.582731.019287.37.3-1.95.9152811.511.5-3.19.583831.519327.37.3-1.95.9153211.511.5-3.19.584932.019367.37.2-1.95.9153611.511.4-3.19.485932.519397.27.2-1.95.9153911.411.4-3.19.4	773	28.5	1910	7.4	7.3	-	1.9	6.0	1510	11.7	11.7	-	3.1	9.6
79529.519187.37.37.3-1.96.0151811.711.6-3.19.680630.019217.37.3-1.96.0152111.611.6-3.19.681730.519257.37.3-1.96.0152511.611.5-3.19.682731.019287.37.3-1.95.9152811.511.5-3.19.583831.519327.37.3-1.95.9153211.511.5-3.19.584932.019367.37.2-1.95.9153611.511.4-3.19.485932.519397.27.2-1.95.9153911.411.4-3.19.4	784	29.0	1914	7.4	7.3	-	1.9	6.0	1514	11.7	11.6	-	3.1	9.6
80630.019217.37.31.96.0152111.611.63.19.681730.519257.37.31.96.0152511.611.53.19.582731.019287.37.31.95.9152811.511.53.19.583831.519327.37.31.95.9153211.511.53.19.584932.019367.37.21.95.9153611.511.43.19.485932.519397.27.21.95.9153911.411.43.19.4	795	29.5	1918	7.3	7.3	-	1.9	6.0	1518	11.7	11.6	-	3.1	9.6
817 30.5 1925 7.3 7.3 - 1.9 6.0 1525 11.6 11.5 - 3.1 9.5 827 31.0 1928 7.3 7.3 - 1.9 5.9 1528 11.5 11.5 - 3.1 9.5 838 31.5 1932 7.3 7.3 - 1.9 5.9 1528 11.5 11.5 - 3.1 9.5 849 32.0 1936 7.3 7.2 - 1.9 5.9 1536 11.5 11.4 - 3.1 9.4 859 32.5 1939 7.2 7.2 - 1.9 5.9 1539 11.4 11.4 - 3.1 9.4	806	30.0	1921	7.3	7.3	-	1.9	6.0	1521	11.6	11.6	-	3.1	9.6
827 31.0 1928 7.3 7.3 - 1.9 5.9 1528 11.5 11.5 - 3.1 9.5 838 31.5 1932 7.3 7.3 - 1.9 5.9 1532 11.5 11.5 - 3.1 9.5 849 32.0 1936 7.3 7.2 - 1.9 5.9 1536 11.5 11.4 - 3.1 9.5 859 32.5 1939 7.2 7.2 - 1.9 5.9 1539 11.4 11.4 - 3.1 9.4	817	30.5	1925	7.3	7.3	-	1.9	6.0	1525	11.6	11.5	-	3.1	9.5
838 31.5 1932 7.3 7.3 - 1.9 5.9 1532 11.5 11.5 - 3.1 9.5 849 32.0 1936 7.3 7.2 - 1.9 5.9 1536 11.5 11.4 - 3.1 9.4 859 32.5 1939 7.2 7.2 - 1.9 5.9 1539 11.4 11.4 - 3.1 9.4	827	31.0	1928	7.3	7.3	-	1.9	5.9	1528	11.5	11.5	-	3.1	9.5
849 32.0 1936 7.3 7.2 - 1.9 5.9 1536 11.5 11.4 - 3.1 9.4 859 32.5 1939 7.2 7.2 - 1.9 5.9 1536 11.5 11.4 - 3.1 9.4	838	31.5	1932	7.3	7.3	-	1.9	5.9	1532	11.5	11.5	-	3.1	9.5
859 32.5 1939 7.2 7.2 - 1.9 5.9 1539 11.4 11.4 - 3.1 9.4	849	32.0	1936	7.3	7.2	-	1.9	5.9	1536	11.5	11.4	-	3.1	9.4
	859	32.5	1939	7.2	7.2	-	1.9	5.9	1539	11.4	11.4	-	3.1	9.4

Table S-1 Calculated $10^3 \ln \beta^{13/12}$ C of carbonates, Fe₃C and diamond along modern mantle and cold slab geotherms (Yang *et al.*, 2017). $10^3 \ln \beta$ of high-spin (HS) and low-spin (LS) FeCO₃ are listed in separate columns with spin transition pressure at ~45 GPa.



869	33.0	1943	7.2	7.2	-	1.9	5.9	1543	11.4	11.4	-	3.1	9.4
880	33.5	1946	7.2	7.2	-	1.9	5.9	1546	11.4	11.3	-	3.1	9.4
890	34.0	1950	7.2	7.2	-	1.9	5.9	1550	11.3	11.3	-	3.1	9.3
900	34.5	1953	7.2	7.2	-	1.9	5.9	1553	11.3	11.3	-	3.1	9.3
910	35.0	1957	7.2	7.1	-	1.9	5.9	1557	11.3	11.2	-	3.0	9.3
923	35.5	1960	7.2	7.1	-	1.9	5.9	1560	11.2	11.2	-	3.0	9.3
935	36.0	1964	71	71	-	19	58	1564	11.2	11.2	-	3.0	92
947	36.5	1967	71	71	_	19	5.8	1567	11.2	11.1	_	3.0	92
959	37.0	1971	71	7.1	_	1.9	5.8	1571	11.2	11.1	_	3.0	9.2
971	37.5	1974	71	71	_	19	5.8	1574	11.1	11.1	_	3.0	92
983	38.0	1977	7.1	7.1	-	1.9	5.8	1577	11.1	11.1	_	3.0	9.1
995	38.5	1981	7.1	7.1	_	1.9	5.8	1581	11.1	11.0	_	3.0	9.1
1007	39.0	1984	7.1	7.1	_	1.9	5.8	1584	11.0	11.0		3.0	9.1
1007	39.5	1988	7.1	7.0		1.9	5.8	1588	11.0	11.0		3.0	9.1
1017	40.0	1001	7.0	7.0	_	1.9	5.8	1501	10.0	10.9	_	3.0	9.1
1042	40.0	1991	7.0	7.0	-	1.9	5.0	1504	10.9	10.9	-	2.0	9.0
1045	40.5	1994	7.0	7.0	-	1.9	5.0	1594	10.9	10.9	-	2.0	9.0
1055	41.0	2001	7.0	7.0	-	1.9	5.7	1601	10.9	10.9	-	3.0	9.0
1067	41.5	2001	7.0	7.0	-	1.9	5.7	1601	10.9	10.8	-	3.0	9.0
1079	42.0	2004	7.0	7.0	-	1.9	5.7	1604	10.8	10.8	-	3.0	9.0
1090	42.5	2008	7.0	6.9	-	1.9	5.7	1608	10.8	10.8	-	3.0	8.9
1102	43.0	2011	6.9	6.9	-	1.9	5.7	1611	10.8	10.8	-	3.0	8.9
1114	43.5	2014	6.9	6.9	-	1.9	5.7	1614	10.7	10.7	-	3.0	8.9
1126	44.0	2017	6.9	6.9	-	1.9	5.7	1617	10.7	10.7	-	3.0	8.9
1137	44.5	2021	6.9	6.9	-	1.9	5.7	1621	10.7	10.7	-	3.0	8.9
1149	45.0	2024	6.9	6.9	6.6	1.9	5.7	1624	10.7	10.7	10.2	3.0	8.8
1161	45.5	2027	6.9	-	6.6	1.9	5.7	1627	10.6	-	10.1	3.0	8.8
1172	46.0	2030	6.9	-	6.5	1.9	5.7	1630	10.6	-	10.1	3.0	8.8
1184	46.5	2034	6.9	-	6.5	1.9	5.6	1634	10.6	-	10.1	3.0	8.8
1195	47.0	2037	6.8	-	6.5	1.9	5.6	1637	10.5	-	10.0	3.0	8.8
1207	47.5	2040	6.8	-	6.5	1.9	5.6	1640	10.5	-	10.0	3.0	8.7
1219	48.0	2043	6.8	-	6.5	1.9	5.6	1643	10.5	-	10.0	3.0	8.7
1230	48.5	2046	6.8	-	6.5	1.9	5.6	1646	10.5	-	10.0	3.0	8.7
1241	49.0	2049	6.8	-	6.5	1.9	5.6	1649	10.4	-	9.9	3.0	8.7
1253	49.5	2053	6.8	-	6.4	1.9	5.6	1653	10.4	-	9.9	2.9	8.7
1264	50.0	2056	6.8	-	6.4	1.9	5.6	1656	10.4	-	9.9	2.9	8.6
1276	50.5	2059	6.8	-	6.4	1.9	5.6	1659	10.4	-	9.9	2.9	8.6
1287	51.0	2062	6.7	-	6.4	1.9	5.6	1662	10.3	-	9.8	2.9	8.6
1298	51.5	2065	6.7	-	6.4	1.9	5.6	1665	10.3	-	9.8	2.9	8.6
1310	52.0	2068	6.7	-	6.4	1.9	5.6	1668	10.3	-	9.8	2.9	8.6
1321	52.5	2071	6.7	-	6.4	1.9	5.6	1671	10.3	-	9.8	2.9	8.5
1332	53.0	2074	6.7	-	6.4	1.9	5.5	1674	10.2	-	9.7	2.9	8.5
1344	53.5	2077	6.7	-	6.4	1.9	5.5	1677	10.2	-	9.7	2.9	8.5
1355	54.0	2080	6.7	-	6.3	1.9	5.5	1680	10.2	-	9.7	2.9	8.5
1366	54.5	2083	6.7	-	6.3	1.9	5.5	1683	10.2	-	9.7	2.9	8.5
1377	55.0	2086	6.7	-	6.3	1.9	5.5	1686	10.1	-	9.6	2.9	8.5
1388	55.5	2089	6.6	-	63	19	5.5	1689	10.1	-	96	29	84
1399	56.0	2092	6.6	-	63	19	5.5	1692	10.1	-	96	29	84
1411	56.5	2095	6.6	_	6.3	19	5.5	1695	10.1	_	96	2.9	84
1422	57.0	2098	6.6	_	6.3	1.9	5.5	1698	10.1	_	9.5	2.9	8.4
1/122	57.5	2101	6.6	_	6.3	1.9	5.5	1701	10.0	_	9.5	2.9	8.4
1433	58.0	2101	6.6	_	6.2	1.9	5.5	1701	10.0	_	9.5	2.7	8.4
1444	50.0 E0 E	2104	6.6	-	6.2	1.9	5.5 E E	1704	10.0	-	9.5	2.9	0.4
1455	50.5	2107	0.0	-	6.2	1.9	5.5 E E	1707	10.0	-	9.5	2.9	0.5
1400	59.0	2110	6.6	-	6.2	1.9	5.5 E E	1710	10.0	-	9.4	2.9	0.5
14//	09.0 60.0	2113	0.0	-	0.2	1.9	5.5 E 4	1/13	9.9	-	9.4	2.9	0.3
1488	60.0	2116	6.5	-	6.2	1.9	5.4	1/16	9.9	-	9.4	2.9	8.3
1499	60.5	2119	6.5	-	6.2	1.9	5.4	1719	9.9	-	9.4	2.9	8.3
1509	61.0	2122	6.5	-	6.2	1.9	5.4	1722	9.9	-	9.4	2.9	8.3
1520	61.5	2125	6.5	-	6.2	1.9	5.4	1725	9.8	-	9.3	2.9	8.3
1531	62.0	2127	6.5	-	6.2	1.9	5.4	1727	9.8	-	9.3	2.9	8.2
1542	62.5	2130	6.5	-	6.2	1.9	5.4	1730	9.8	-	9.3	2.9	8.2
1553	63.0	2133	6.5	-	6.1	1.9	5.4	1733	9.8	-	9.3	2.9	8.2
1563	63.5	2136	6.5	-	6.1	1.9	5.4	1736	9.8	-	9.2	2.9	8.2



1574	64.0	2139	6.5	-	6.1	1.9	5.4	1739	9.7	-	9.2	2.9	8.2
1585	64.5	2142	6.5	-	6.1	1.9	5.4	1742	9.7	-	9.2	2.9	8.2
1596	65.0	2144	6.4	-	6.1	1.9	5.4	1744	9.7	-	9.2	2.9	8.2
1606	65.5	2147	6.4	-	6.1	1.9	5.4	1747	9.7	-	9.2	2.9	8.1
1617	66.0	2150	6.4	-	6.1	1.9	5.4	1750	9.7	-	9.1	2.9	8.1
1627	66.5	2153	6.4	-	6.1	1.9	5.4	1753	9.6	-	9.1	2.9	8.1
1638	67.0	2155	6.4	-	6.1	1.9	5.4	1755	9.6	-	9.1	2.9	8.1
1649	67.5	2158	6.4	-	6.1	1.9	5.4	1758	9.6	-	9.1	2.9	8.1
1659	68.0	2161	6.4	-	6.0	1.9	5.3	1761	9.6	-	9.1	2.9	8.1
1670	68.5	2164	6.4	-	6.0	1.9	5.3	1764	9.6	-	9.0	2.9	8.1
1680	69.0	2166	6.4	-	6.0	1.9	5.3	1766	9.5	-	9.0	2.9	8.0
1691	69.5	2169	6.4	-	6.0	1.9	5.3	1769	9.5	-	9.0	2.9	8.0
1701	70.0	2172	6.4	-	6.0	1.9	5.3	1772	9.5	-	9.0	2.9	8.0

Table S-2 Fitted parameters for the depth-dependence of $10^{3}\ln\beta^{13}/^{12}$ C of major carbon species along geotherms of modern mantle and cold slab (Yang *et al.*, 2016). ($10^{3}\ln\beta^{13}/^{12}$ C = $a_0 + a_1x + a_2x^2 + a_3x^3$, where x is depth in km). The pressure of Fe²⁺ spin transition in FeCO₃ is set to 45 GPa, corresponding to 1150 km.

Slab	a ₀	a 1	a ₂	a ₃
Fe ₃ C	4.269(4)	-2.64(3)e ⁻³	1.84(4)e-6	-4.6(6)e ⁻¹⁰
HS FeCO ₃	17.3(1)	-1.15(3)e ⁻²	6.5(4)e ⁻⁶	-1.3(2)e ⁻⁹
LS FeCO ₃	14.2(1)	-4.73(1)e ⁻³	1.217(6)e ⁻⁶	-1.38(1)e ⁻¹⁰
MgCO ₃	17.46(3)	-1.19(1)e ⁻²	7.1(1)e ⁻⁶	-1.70(4)e ⁻⁹
Diamond	14.29(3)	-9.86(9)e ⁻³	6.1(1)e ⁻⁶	-1.48(3)e-9
Normal Mantle	\mathbf{a}_0	a 1	a ₂	a ₃
Fe ₃ C	2.340(4)	-1.06(2)e ⁻³	8.0(2)e ⁻⁷	-1.99(6)e ⁻¹⁰
HS FeCO ₃	9.64(1)	-4.19(4)e ⁻³	1.58(3)e-6	0
LS FeCO3	8.254(1)	-1.769(2)e ⁻³	2.630(8)e-7	0
MgCO ₃	9.85(1)	-5.09(5)e ⁻³	3.01(5)e ⁻⁶	-7.3(2)e ⁻¹⁰
Diamond	7.99(1)	-4.22(4)e ⁻³	2.64(5)e ⁻⁶	-6.4(2)e ⁻¹⁰



Supplementary Figures



Figure S-1 The 1-bar ${}^{13}C/{}^{12}C$ β -factors of major C-bearing minerals. The solid curves are for FeCO₃ (red), MgCO₃ (black), CaCO₃ (green) and diamond (blue) calculated by this study. The green dashed curve with open triangles for CaCO₃ and the pink dashed curve for ferromagnetic-Fe₃C are calculated by Horita and Polyakov (2015). The blue dashed curve for diamond is calculated by Polyakov and Kharlashina (1995).





Figure S-2 Synchrotron Mössbauer spectra (SMS) of $FeCO_3$ showing spin transition of Fe^{2+} between 43-46 GPa and 300 K. (a) SMS of $FeCO_3$ collected at 1 bar to 61.7 GPa and 300 K. The white cycles are raw data and black curves are the fitting curves. (b) Representative energy-domain spectra calculated from the fitting results of the SMS spectra by CONUSS (Sturhahn, 2000). Before the spin transition, a doublet is used to fit the spectra, and the asymmetry is likely due to polarisation of the synchrotron Mössbauer source (Cerantola *et al.*, 2015); a double (red) and a singlet (blue) are employed to fit the SMS spectra within the spin transition pressure; a singlet is used for spectra at pressures higher than the spin transition pressure (~46 GPa).



Figure S-3 The FeCO₃ sample in a diamond anvil cell transforms from transparent to opaque between 43.4 and 46.3 GPa, indicating a transition of Fe^{2+} from high-spin state (1 bar – 43.4 GPa) to mixed-spin state (43.4–46.3 GPa) and finally to low-spin state (>46.3 GPa).





Figure S-4 Pressure-dependence of unit-cell volume (a), the average lengths of Fe-O bonds (b) and C-O bonds (c) in FeCO₃. The open and filled circles with fitting curves are for high-spin and low-spin states of Fe^{2+} , respectively, which are calculated using DFT+*U* by this study; the open blue triangles are experimental results from single-crystal XRD measurements (Lavina *et al.*, 2010).





Figure S-5 The ${}^{13}C/{}^{12}C\beta$ -factors of Fe₃C (red curves), MgCO₃ (green curves) and FeCO₃ (blue curves by this study; Fe₃C by Horita and Polyakov (2015, black curves, only temperature effect is considered) along geotherms (Yang *et al.*, 2017) of modern mantle (dashed curves) and cold slab (solid curves). The discontinuities in FeCO₃ curves are caused by spin transition of Fe²⁺.





Figure S-6 Equilibrium ¹³C/¹²C isotopic fractionation between diamond and sourcing carbonate/carbide along modern mantle geotherm (**a**), and cold slab geotherm (**b**) (Yang *et al.*, 2017). As the Archean mantle geotherm may be comparable with current normal geotherm (Santosh *et al.*, 2010), (b) may be also applicable for Archaean diamonds. The discontinuity for $\Delta^{13}C^{\text{Dia-FeCO}_3}$ (red curves) around 50 GPa is due to spin transition of Fe²⁺ in FeCO₃. The black dashed curves are for $\Delta^{13}C^{\text{Dia-FeCO}_3}$. Pressure-driven magnetic and spin transitions in Fe₃C makes the non-magnetic state stable in most parts of the mantle (Lin *et al.*, 2004; Gao *et al.*, 2008), therefore only non-magnetic Fe₃C (blue curves) is considered here. For the pink dotted curves, 1-bar ¹³C/¹²C β -factors of Fe₃C reported by Horita and Polyakov (2015) are used for calculating $\Delta^{13}C^{\text{Dia-Fe₃C}}$ with only temperature effect but no pressure correction.

Letter



Figure S-7 The cumulative distribution functions (CDFs) of δ^{13} C of super-deep diamonds forming from a Fe-C melt source. The red, green and black solid curves are CDFs at depths 250 km, 660 km and 1500 km depths along cold slab geotherm (Yang *et al.*, 2017), respectively. The yellow dotted curve is calculated by using Δ^{13} C^{Dia-FeC} melt at 250 km along modern mantle geotherm (Yang *et al.*, 2017). The pink dashed curve is for diamonds forming from C-O-H fluid (Cartigny *et al.*, 2014). The inset figure shows the CDFs for δ^{13} C of diamonds ranging from -60 ‰ to -25 ‰.





Figure S-8 Nuclear resonant inelastic X-ray scattering (NRIXS) spectra of FeCO₃ up to 61.3 GPa and 300 K. Significant changes in inelastic peaks happens around 46 GPa as a result of spin transition of Fe²⁺.





Figure S-9 A comparison between the distribution of δ^{13} C of eclogitic diamonds and δ^{13} C of diamonds forming from carbonate sources at depths. The histogram for δ^{13} C of eclogitic diamonds (Cartigny *et al.*, 2014) plotted to the left axis; calculated δ^{13} C of diamonds as a function of depths from reduction of MgCO₃ (solid curves) and FeCO₃ (dashed curves) with initial δ^{13} C as 0 ‰ plotted to the right axis. The C isotopic fractionation between solids is calculated by using a Rayleigh distillation model with the conservation of bulk δ^{13} C (Eq. S-4 in SI text) along an expected geotherms of modern mantle and cold slab (Yang *et al.*, 2017), respectively. The residual C fraction (*f*) in MgCO₃ or FeCO₃ is 0.1 for the green solid and black dashed curves; *f* equals 0.9 for the red solid and blue dashed curves.



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