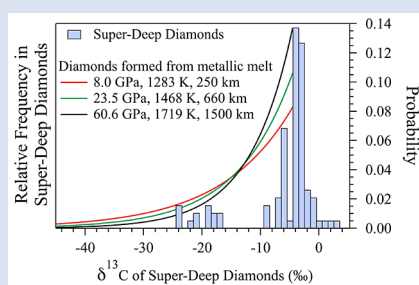# Carbon isotopic signatures of super-deep diamonds mediated by iron redox chemistry

J. Liu[1]*, W. Wang[2]*, H. Yang[3], Z. Wu[2,4]*, M.Y. Hu[5], J. Zhao[5],
W. Bi[5,6], E.E. Alp[5], N. Dauphas[7], W. Liang[8], B. Chen[9], J.-F. Lin[1]*

OPEN ACCESS

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 Fe_3C 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 Fe_3C 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 CH_4 or CO_2-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 CH_4 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 CO_2 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.

1. Department of Geological Sciences, Jackson School of Geosciences, University of Texas at Austin, Austin, Texas 78712, USA
2. Laboratory of Seismology and Physics of Earth's Interior, School of Earth and Space Sciences, University of Science and Technology of China, Hefei, China
3. Center for High Pressure Science and Technology Advanced Research (HPSTAR), Pudong, Shanghai 201203, China
4. CAS Center for Excellence in Comparative Planetology, China
5. Advanced Photon Source, Argonne National Laboratory, Argonne, Illinois 60439, USA
6. Department of Geology, University of Illinois at Urbana-Champaign, Urbana, Illinois 61801, USA
7. Origins Laboratory, Department of the Geophysical Sciences and Enrico Fermi Institute, The University of Chicago, 5734 South Ellis Avenue, Chicago, Illinois 60637, USA
8. Key Laboratory for High Temperature and High Pressure Study of the Earth's Interior, Institute of Geochemistry, Chinese Academy of Sciences, Guiyang, Guizhou 550002, China
9. Hawaii Institute of Geophysics and Planetology, University of Hawaii at Manoa, Honolulu, HI 96822, USA
*   Corresponding author (email: jiacliu@utexas.edu; afu@jsg.utexas.edu; wuzq10@ustc.edu.cn; wz30304@mail.ustc.edu.cn)

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):

$$3FeO = Fe + Fe_2O_3 \qquad \text{Eq. 1}$$

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):

$$FeCO_3 + 2Fe = 3FeO + C \qquad \text{Eq. 2}$$

$$FeCO_3 + 5Fe = 3FeO + Fe_3C \qquad \text{Eq. 3}$$
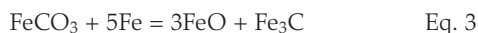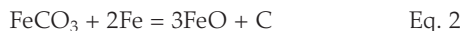
Fe_3C can also serve as a reduced C source to form diamonds through the following redox reaction (Bataleva *et al.,* 2016):

$$Fe_3C + 3Fe_2O_3 = 9FeO + C \qquad \text{Eq. 4}$$

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:

$$Fe\text{-}C \text{ melt} + Fe_2O_3 = 3FeO + C \qquad \text{Eq. 5}$$

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_3C 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,

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

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 $MgCO_3$, $FeCO_3$, Fe_3C 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_3C (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 bound length is lengthened by 2.1 % (Fig. S-4). The magnetic state of Fe_3C 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_3C 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 $\Delta C^{Dia\text{-}Fe_3C}$ is larger than other inter-mineral fractionations involving diamond, such as $\Delta C^{Dia\text{-}Carbonates}$ (Fig. S-6). Our calculated $\Delta C^{Dia\text{-}Fe_3C}$ 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 $\Delta C^{Dia\text{-}Fe_3C}$ reported by Horita and Polyakov (2015). Therefore the 1-bar data would overestimate the C isotopic fractionation during diamond formation from a Fe_3C 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, $\Delta^{13}C^{Dia\text{-}FeC \text{ melt}}$ is calculated by the sum of $\Delta^{13}C^{Dia\text{-}Fe_3C}$ (Fig. S-6) and the equilibrium fractionation $\Delta^{13}C^{Fe_3C\text{-}FeC \text{ melt}} = -5.6 \times 10^6/T^2$ anchored to the experimentally determined value of ~-2 ‰ at 6.3 GPa and 1673 K (Reutsky *et al.,* 2015). By using this calculated $\Delta^{13}C^{Dia\text{-}FeC \text{ melt}}$, $\delta^{13}C$ 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.
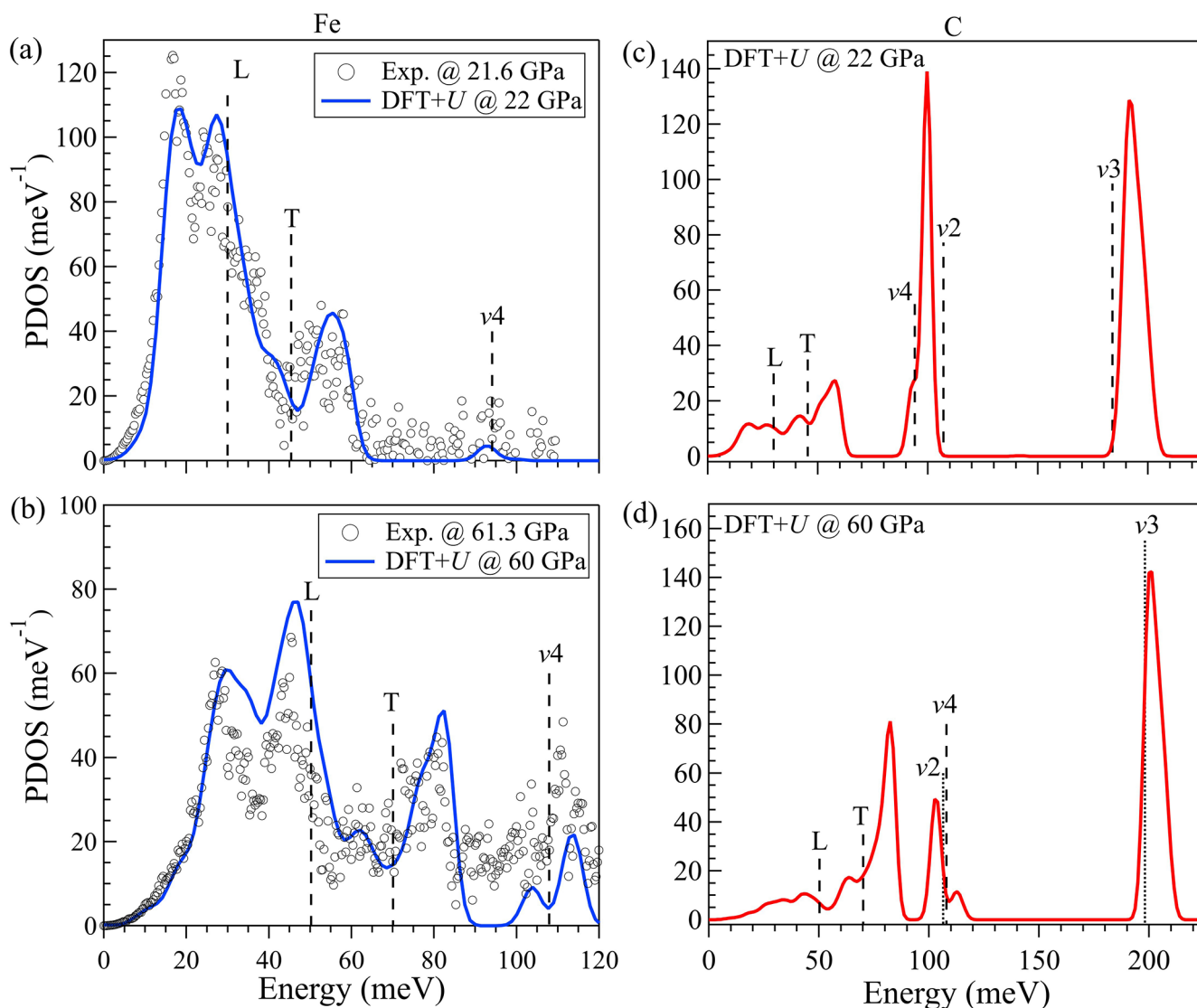
Figure 1 Partial phonon density of states (PDOS) of ^{57}Fe **(a, b)** and ^{12}C **(c, d)** in FeCO$_3$ at high pressures. In **(a)** and **(b)**, the open cycles are PDOS of Fe measured by NRIXS; the blue curves are calculated PDOS of Fe by DFT + U. The red curves in **(c)** and **(d)** are calculated 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 FeCO$_3$ (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 CO$_3^{2-}$ (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 FeCO$_3$ (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 Fe^{2+} and neighbouring CO$_3^{2-}$ units.

The probability density function (PDF) of $\delta^{13}C^{Dia}$ values of diamond formed from metallic melt, which we note as $g(\delta^{13}C^{Dia})$, is simply given as below (see detailed derivation in *Supplementary Information*),

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

The PDFs for $\Delta^{13}C^{Dia\text{-}Fe_3C}$ at representative upper mantle, transition zone, and lower mantle depths are shown in Figure 2. For each PDF, $\delta^{13}C_0^{Source}$ is set to locate the maximum probability of $\delta^{13}C^{Dia}$ at -5 ‰, which is the mode of $\delta^{13}C$ of worldwide diamonds (Cartigny et al., 2014). Because of the decrease of $\Delta^{13}C^{Dia\text{-}FeC\ melt}$ 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 $\delta^{13}C^{Dia}$ 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 $\delta^{13}C$ 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.
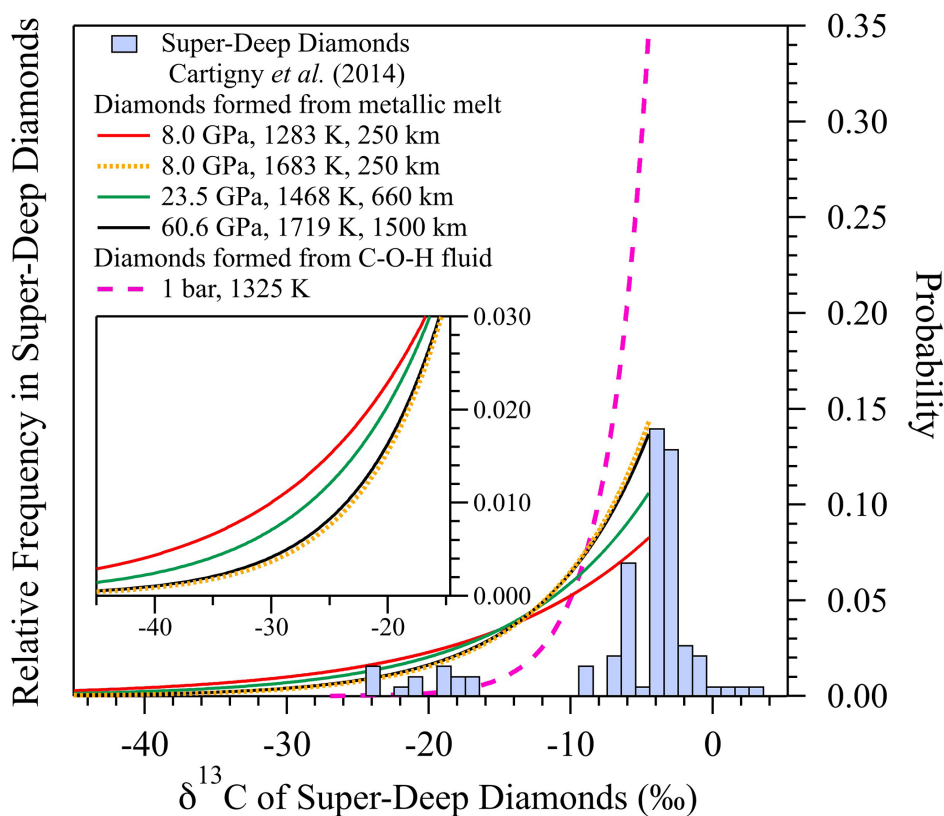
Figure 2   Comparison of the histogram for $\delta^{13}C$ of super-deep diamonds (left axis) and the probability density functions (PDFs, right axis) of $\delta^{13}C^{Dia}$ derived from metallic melt for different *P-T* conditions. The red, green and black solid curves are calculated PDFs by using $\Delta^{13}C^{Dia-FeC\ melt}$ 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 $\Delta^{13}C^{Dia-FeC\ melt}$ 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 $\Delta^{13}C^{Dia-COH}$ (-2.9 ‰) (Cartigny *et al.*, 2014). The inset figure shows the negative tailings of these three PDFs. $\delta^{13}C$ data of super-deep diamonds are from Cartigny *et al.* (2014).

Acknowledgements

Editor: Wendy Mao

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

References

ANZOLINI, C. *ET AL.* (2019) Depth of diamond formation obtained from single periclase inclusions. *Geology* 47, 219–222.

BATALEVA, Y.V., PALYANOV, Y.N., BORZDOV, Y.M., BAYUKOV, O.A., SOBOLEV, N.V. (2015) Interaction of iron carbide and sulfur under P–T conditions of the lithospheric mantle. *Doklady Earth Sciences* 463, 707–711.

BATALEVA, Y.V., PALYANOV, Y.N., BORZDOV, Y.M., BAYUKOV, O.A., SOBOLEV, N.V. (2016) Conditions for diamond and graphite formation from iron carbide at the P-T parameters of lithospheric mantle. *Russian Geology and Geophysics* 57, 176–189.

CARTIGNY, P., PALOT, M., THOMASSOT, E., HARRIS, J.W. (2014) Diamond Formation: A Stable Isotope Perspective. *Annual Review of Earth and Planetary Sciences* 42, 699–732.

DAUPHAS, N., HU, M.Y., BAKER, E.M., HU, J., TISSOT, F.L.H., ALP, E.E., ROSKOSZ, M., ZHAO, J., BI, W., LIU, J., J.-F., NIEA, N.X., HEARD, A. (2018) SciPhon: a data analysis software for nuclear resonant inelastic X-ray scattering with applications to Fe, Kr, Sn, Eu and Dy. *Journal of Synchrotron Radiation* 25, 1581–1599.

DE STEFANO, A., KOPYLOVA, M.G., CARTIGNY, P., AFANASIEV, V. (2009) Diamonds and eclogites of the Jericho kimberlite (Northern Canada). *Contributions to Mineralogy and Petrology* 158, 295–315.

FROST, D.J., LIEBSKE, C., LANGENHORST, F., McCAMMON, C.A., TRONNES, R.G., RUBIE, D.C. (2004) Experimental evidence for the existence of iron-rich metal in the Earth's lower mantle. *Nature* 428, 409–412.

GALIMOV, E.M. (1991) Isotope fractionation related to kimberlite magmatism and diamond formation. *Geochimica et Cosmochimica Acta* 55, 1697–1708.

GAO, L., CHEN, B., WANG, J., ALP, E.E., ZHAO, J., LERCHE, M., STURHAHN, W., SCOTT, H.P., HUANG, F., DING, Y., SINOGEIKIN, S.V., LUNDSTROM, C.C., BASS, J.D., LI, J. (2008) Pressure-induced magnetic transition and sound velocities of Fe_3C: Implications for carbon in the Earth's inner core. *Geophysical Research Letters* 35, L17306.

GIANNOZZI, P., BARONI, S., BONINI, N., CALANDRA, M. , CAR, R., ET AL. (2009) QUANTUM ESPRESSO: a modular and open-source software project for quantum simulations of materials. *Journal of Physics: Condensed Matter* 21, 395502.

HORITA, J., POLYAKOV, V.B. (2015) Carbon-bearing iron phases and the carbon isotope composition of the deep Earth. *Proceedings of the National Academy of Sciences* 112, 31–36.

KAMINSKY, F.V., WIRTH, R. (2011) Iron Carbide Inclusions in Lower-Mantle Diamond from Juina, Brazil. *Canadian Mineralogist* 49, 555–572.

KOGA, K.T., WALTER, M.J., NAKAMURA, E., KOBAYASHI, K. (2005) Carbon self-diffusion in a natural diamond. *Physical Review B* 72, 024108.

LIN, J.-F., STRUZHKIN, V.V., MAO, H., HEMLEY, R.J., CHOW, P., HU, M.Y., LI, J. (2004) Magnetic transition in compressed Fe_3C from x-ray emission spectroscopy. *Physical Review B* 70, 212405.

LIN, J.-F., LIU, J., JACOBS, C., PRAKAPENKA, V.B. (2012) Vibrational and elastic properties of ferromagnesite across the electronic spin-pairing transition of iron. *American Mineralogist* 97, 583–591.

LIU, J., LI, J., HRUBIAK, R., SMITH, J.S. (2016) Origins of ultralow velocity zones through slab-derived metallic melt. *Proceedings of the National Academy of Sciences* 113, 5547–5551.

MIKHAIL, S., GUILLERMIER, C., FRANCHI, I.A., BEARD, A.D., CRISPIN, K., VERCHOVSKY, A.B., JONES, A.P., MILLEDGE, H.J. (2014) Empirical evidence for the fractionation of carbon isotopes between diamond and iron carbide from the Earth's mantle. *Geochemistry, Geophysics, Geosystems* 15, 855–866.

PALYANOV, Y.N., BATALEVA, Y.V., SOKOL, A.G., BORZDOV, Y.M., KUPRIYANOV, I.N., REUTSKY, V.N., SOBOLEV, N.V. (2013) Mantle-slab interaction and redox mechanism of diamond formation. *Proceedings of the National Academy of Sciences of the United States of America* 110, 20408–20413.

REUTSKY, V.N., BORZDOV, Y.M., PALYANOV, Y.N. (2015) Carbon isotope fractionation during high pressure and high temperature crystallization of Fe–C melt. *Chemical Geology* 406, 18–24.

ROHRBACH, A., BALLHAUS, C., GOLLA–SCHINDLER, U., ULMER, P., KAMENETSKY, V.S., KUZMIN, D.V. (2007) Metal saturation in the upper mantle. *Nature* 449, 456–458.

ROHRBACH, A., GHOSH, S., SCHMIDT, M.W., WIJBRANS, C.H., KLEMME, S. (2014) The stability of Fe–Ni carbides in the Earth's mantle: Evidence for a low Fe–Ni–C melt fraction in the deep mantle. *Earth and Planetary Science Letters* 388, 211–221.

SANTILLÁN, J., WILLIAMS, Q. (2004) A high-pressure infrared and X-ray study of $FeCO_3$ and $MnCO_3$: comparison with $CaMg(CO_3)_2$-dolomite. *Physics of the Earth and Planetary Interiors* 143–144, 291–304.

SANTOSH, M., MARUYAMA, S., KOMIYA, T., YAMAMOTO, S. (2010) Orogens in the evolving Earth: from surface continents to 'lost continents' at the core–mantle boundary. *Geological Society, London, Special Publications* 338, 77–116.

SMART, K.A., CHACKO, T., STACHEL, T., MUEHLENBACHS, K., STERN, R.A., HEAMAN, L.M. (2011) Diamond growth from oxidized carbon sources beneath the Northern Slave Craton, Canada: A $\delta^{13}C$–N study of eclogite-hosted diamonds from the Jericho kimberlite. *Geochimica et Cosmochimica Acta* 75, 6027–6047.

SMITH, E.M., SHIREY, S.B., NESTOLA, F., BULLOCK, E.S., WANG, J.H., RICHARDSON, S.H., WANG, W.Y. (2016) Large gem diamonds from metallic liquid in Earth's deep mantle. *Science* 354, 1403–1405.

WALTER, M.J., KOHN, S.C., ARAUJO, D., BULANOVA, G.P., SMITH, C.B., GAILLOU, E., WANG, J., STEELE, A., SHIREY, S.B. (2011) Deep Mantle Cycling of Oceanic Crust: Evidence from Diamonds and Their Mineral Inclusions. *Science* 334, 54–57.

YANG, D., WANG, W., WU, Z. (2017) Elasticity of superhydrous phase B at the mantle temperatures and pressures: Implications for 800 km discontinuity and water flow into the lower mantle. *Journal of Geophysical Research: Solid Earth* 122, 5026–5037.