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# Carbon isotopic signatures of diamond formation mediated by iron redox chemistry

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Diamonds are key messenger from the deep Earth because some are sourced from the longest isolated and deepest accessible regions of the Earth's mantle. They are prime recorders of the carbon isotopic composition of the Earth. The C isotope composition ($d^{13}C$) of natural diamonds shows a wide variation from -41 ‰ to +3 ‰ with the primary mode at -5 ± 3 ‰ [1]. In comparison, the $d^{13}C$ values of chondrites and other planetary bodies range between -26 ‰ and -15 ‰ [2]. It is possible that some of the low $d^{13}C$ values were inherited from the Earth's building blocks, but this is unlikely to be the sole explanation for all low $d^{13}C$ values that can reach as low as -41 ‰. Organic matter at the Earth's surface that has low $d^{13}C$ values [3] has been regarded as a possible origin for low $d^{13}C$ values. However, organic carbon is usually accompanied by carbonate with higher $d^{13}C$ values (~0 ‰), and it is not clear why this $d^{13}C$ value does not appear frequently in diamonds. Low $d^{13}C$ diamonds were also formed by deposition from C-O-H fluids, but the equilibrium fractionation involved between diamonds and fluids is small at mantle temperatures [1] and the low $d^{13}C$ values of diamonds can only be achieved after extensive Rayleigh distillation.

One unique feature of the Earth is active plate tectonics driven by mantle convection. Relatively oxidized iron and carbon species at the surface, such as carbonate, $Fe^{2+}$- and $Fe^{3+}$-bearing silicates and oxides, are transported to the deep mantle by subducted slabs and strongly involved in the redox reactions that generate diamonds [4]. The extent to which the isotopic composition of C during diamond formation records redox processes that shaped the Earth is still controversial. Here we report on vibration properties of C and Fe at high pressure in carbonates, diamond and $Fe_3C$, based on nuclear resonant inelastic X-ray scattering measurements and density functional theory calculations and further calculate equilibrium C isotope fractionations among these C-bearing species. Our results demonstrate that redox reactions in subducted slabs could generate eclogitic diamonds with $d^{13}C$ values as low as -41 ‰ if C in diamonds was sourced from the oxidation of a Fe-C liquid. The large C isotopic fractionation and potentially fast separation between diamonds and a Fe-C melt could enable diamond formation as high as 2 % with $d^{13}C$ lower than -40 ‰.

### References

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