

## Carbon isotope fractionation during HPHT crystallization of Fe-C melt

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Carbides are one of the major host of carbon in reduced part of the Earth's mantle [1]. However, nothing is known about carbon isotope fractionation during carbide formation. Restricted data on comparison of isotope compositions of graphite(diamond) and carbides (cohenite, taenite) in meteorites show the difference up to 15‰. Experimental attempts on determination of diamond-carbide isotope effects [2,3] have been inhibited by methodological and HPHT technique related uncertainties. Moreover, diamond-carbide approach is not fully adequate for solving the question about isotope fractionation at carbide formation. Both diamond and carbide are growing from metal-carbon melt and the difference between these crystal phases not saying much about crystal-liquid effects. Here we present distribution of carbon isotopes between diamond, iron carbide and quenched rest of Fe-C melt obtained from HPHT crystallization experiments.

Experiments were done at 5.7GPa and 1400°C with slow cooling down to 1300°C during 3 hrs. Initial mix of iron metal (grade 99,998) and graphite ( $\delta^{13}\text{C}=23,0\text{‰}$ ) of  $\text{Fe}_3\text{C}$  stoichiometric composition was transformed to diamond crystals and  $\text{Fe}_3\text{C}$  crystalline aggregate. About 20% of Fe-C melt was quenched forming fine iron-carbide aggregate. Isotope measurements were done as described in [4].

$\delta^{13}\text{C}$  values of diamond crystals (-20,3...-22,2) appear to be higher than initial composition, confirming isotope fractionation at diamond crystallization.  $\text{Fe}_3\text{C}$  aggregate has  $\delta^{13}\text{C}$  values lower than the initial ratio and shows isotope trends in directions of growth from 24,9 down to 27,0. The trends are in agreement with Rayleigh's condensational depletion. Direct measurements of  $\text{Fe}_3\text{C}$  and quenched Fe-C melt nearby phase's boundary reveal 2,2‰ enrichment of carbide with  $^{13}\text{C}$  isotope. Overall distribution of carbon isotopes is best fit with numerical modeling of isotope depletion during crystallization of diamond (isotope effect 4,5‰) followed by carbide growth (isotope effect 2,2‰).

Carbide crystallization at depth relevant to PT-conditions of our experiments is widely suggested [1,5]. Iron carbides can crystallize during co-called RedOx freezing. Reaction zones between mantle domains with contrast  $f\text{O}_2$  are believed to consist of iron carbides. Following our experiments, such iron carbide zones will have pronounced carbon isotope gradients if crystallize from Fe-C melt. Further processing of such carbide into diamond as a result of RedOx freezing process will highlights the inhomogeneity and leads to isotope trends or zoning in resulting diamond crystals. Because of extremely low carbon isotope diffusion in diamond [6], the isotope inhomogeneity is preserved in geological timescale. Thus, in some cases inner carbon isotope inhomogeneity of natural diamonds could be result of iron carbide crystallization form Fe-C melt and have no connection with changing of carbon sources. Work is supported by RFBR (12-05-00846) and SB RAS (project 31).

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