

Polycrystalline diamonds witness redox processes in the Earth's mantle

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Polycrystalline diamond aggregates (framesites) from the Orapa kimberlite (Botswana) contain a syngenetic micro- and nano-inclusion suite of magnetite, pyrrhotite, omphacite, garnet, rutile and C-O-H fluid in order of abundance. This suite of inclusions is distinctly different from those in fibrous diamonds, although the presence of sub-micrometer fluid inclusions provides evidence for a similarly important role of fluids in the genesis of polycrystalline diamond. High resolution μ -Computed Tomography (resolution $1.3\mu\text{m}$ per voxel) combined with Focused Ion Beam assisted Transmission Electron Microscopy reveals epigenetic replacement coatings of hematite and late stage sheet silicates around magnetites showing that magnetites are often (but not always) interstitial to the diamond and, thus, were open to late stage more oxidized overprinting. We present evidence that the primary paragenesis preceding this late stage event formed from a reduced, water-rich C-O-H fluid oversaturated in carbon upon entering the base of the subcratonic lithosphere along opening cracks. Precipitation of diamond increased the water content of the fluid, fluxing melting of surrounding rocks (eclogitic silicates, Fe-sulfides, oxides), which reprecipitated in the interstices between diamonds and as nano-inclusions. Pyrrhotite crystallization led to a rise in $f\text{O}_2$ in the small-scale Fe-O-S melt, which is amplified by the precipitation of diamond from the C-O-H fluid, moving the whole system towards more oxidizing conditions. Thus, $f\text{O}_2$ conditions were more reducing at the start of diamond precipitation and evolved towards more oxidizing conditions upon cooling and solidification. The inclusion paragenesis was generated in a local small-scale equilibrium system, and is representative only for the redox conditions towards the end of diamond precipitation. It is generally acknowledged that sulfide melts are relatively immobile in the Earth's mantle. Formation of polycrystalline diamond would require only local remobilization and small-scale transport of pre-existing material. Cratonic roots have been episodically impregnated with carbon-rich fluids - small volume melts from mantle sources as well as subducted basaltic material - since Archean times. This process leads to diamond formation at a range of spatial scales.

Diamond-graphite transformation: A NanoSIMS isotope study of diamond-graphite inclusion in zircon from the Kochetav massif

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Diamond from ultrahigh-pressure metamorphic terrains (UHPM) is an important mineralogical indicator of deep lithospheric slab subduction (>150 km) into Earth's mantle. Details about diamond-to-graphite transition occurring during subsequent exhumation are not well understood. Because the structures of diamond and graphite are so dissimilar, it is unlikely that a direct phase transformation would occur in the graphitization process. Heating experiments at $T=1500\text{-}1800^\circ\text{C}$ and ambient pressure showed that diamond is replaced by disordered graphite along planes with a high concentration of dislocations.

In order to better understand the process of diamond-to-graphite transformation we measured C, and N isotopes in an inclusion, comprising graphite with a diamond core, in zircon from the Kochetav massif, Kazakhstan. The inclusion is $\sim 10\mu\text{m}$ in diameter and consists of a $\sim 3\mu\text{m}$ diamond core that is surrounded by a graphite rim $\sim 7\mu\text{m}$ in thickness. The C and N isotopes were measured with a Cameca NanoSIMS-50. Diamond and graphite in the inclusion are isotopically indistinguishable (i.e. $\Delta^{13}\text{C}_{\text{diamond-graphite}}$ and $\Delta^{15}\text{N}_{\text{diamond-graphite}} \approx 0$). The C and N isotopic composition for the entire inclusion is $\delta^{13}\text{C} = -30 \pm 1\text{‰}$ and $\delta^{15}\text{N} = +0.5 \pm 3\text{‰}$ respectively, which is in the range of carbon of organic origin.

The distinctive geometry of the diamond-graphite inclusion - the diamond core mantled by graphite - suggests a retrogressive reaction that probably occurred due to decompression during the host rock's exhumation to the Earth's surface from depths > 120-150 km. The lack of intra-mineral isotope fractionation between diamond and graphite for both C and N isotopes suggests that the retrogressive diamond-to-graphite transformation occurred at temperatures above 500°C and pressures less than 4 GPa. Raman spectroscopy studies of this diamond by Smith *et al.* (2011) show the presence of 1624 -1647 cm^{-1} bands which are close to those of disordered graphite. We thus hypothesize that during exhumation diamond was gradually replaced by graphite through an intermediate phase of disordered graphite.