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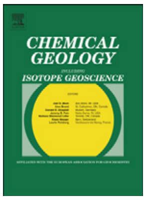

An eclogitic diamond from Mir pipe (Yakutia), recording two growth events from different isotopic sources

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ABSTRACT

An eclogitic octahedral macrodiamond from the Mir kimberlite (Yakutia) has a complex growth structure with distinctive core, intermediate and rim zones. Carbon isotope ratios change abruptly from depleted $\delta^{13}C$ values of −16.6‰ in the core to a mean mantle-like signature of −6.8‰ in the intermediate and −7.5‰ in the rim areas, establishing that two main stages of diamond formation took place from fluids/melts derived from different carbon isotope reservoirs. The core and intermediate growth areas are separated by a zone with oscillatory growth that records an episode of diamond dissolution and regrowth. The Mir kimberlite pipe is known to contain two populations of eclogitic diamonds, with light and heavy carbon isotopes, but this is the first case where both populations have been found in a single diamond monocrystal.

Multiple sulphides and two silicate inclusions occur at the boundary of the oscillatory zone with the intermediate area of the diamond. Silicate inclusions are composite and there is textural and compositional disequilibrium between the mineral phases. A primary omphacite phase has Mg# 66, a high jadeite content, 0.3 wt.% K_2O and contains no Cr. Texturally later omphacites in the composite inclusions have Mg# 70, lower jadeite, no potassium, 0.3 wt.% Cr_2O_3 and occur together with interstitial albite and single grains of phlogopite. Late omphacites are 1.6–3 times higher in Ba, Ti, and Yb. This later mineral assemblage was formed as the result of decompression of primary omphacite in a partly open system in the presence of a fluid/melt enriched in Ba, K, Ti, Yb, Cr, and possibly water. Estimated formation pressure for the primary omphacite based on experimental data is 6 GPa and significantly less than 6 GPa for the later omphacites.

A mantle residence time of 1.7 Ga is implied for the core formation of the studied diamond, using published results that couple a 2.1 Ga Re–Os sulphide inclusion age for Mir eclogitic diamonds with $\delta^{13}C$ values of <−10‰, relative to the 0.36 Ga emplacement age of the kimberlite. The re-growth and formation of the intermediate and rim areas took place at 0.9 Ga based on a Re–Os isochron age determined from the sulphide inclusions of these zones, from a carbon source with mean mantle $\delta^{13}C$ values.

It is proposed that an early eclogitic diamond population characterised by low N content, negative $\delta^{15}N$ and low $\delta^{13}C$ values formed at a mantle depth of ~180 km during the final assembly of the Siberian Craton associated with active subduction at ~2.1 Ga. Formation of the second, 0.9 Ga aged population of eclogitic diamonds characterised by moderate N content, less negative $\delta^{15}N$ and typical mean-mantle $\delta^{13}C$ values (−5‰) took place at a shallower depth of ~120 km and is associated with rift-related magmatism at the end of the Proterozoic. Evidence for both episodes of Mir eclogitic diamond growth is found recording its exhumation from lower to shallower upper mantle depths and formation in two distinct geochemical environments.

1. Introduction

Natural diamond is a high pressure–temperature mineral that can remain unchanged within the mantle for billions of years recording the presence and nature of past deep mantle carbon (e.g., Pearson and Shirey, 1999). Hence, diamonds brought to the surface by kimberlite magmas preserve pristine geochemical and petrological information on Earth's ancient history related to the formation and evolution of

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the early mantle and crust (Richardson et al., 1984; Pearson et al., 2003; Shirey et al., 2004). Syngenetic mineral inclusions in diamonds (Futergendler and Frank-Kamenetsky, 1961; Wiggers de Vries et al., 2011) derived from the upper mantle have two main geochemical affinities: peridotitic (P-type) and eclogitic (E-type) (Meyer and Boyd, 1972; Sobolev, 1974), although a minor websteritic suite intermediate between P and E compositions is also recognised (Stachel and Harris, 2008). Kimberlitic diamonds of all parageneses are xenocrysts derived from diamondiferous eclogites and peridotites, from which they are liberated during transport to the surface via kimberlite magmatism (Bonney, 1899; Sobolev, 1974; Robinson, 1978).

Peridotitic diamonds (P-Type) have distinctive geochemical characteristics that are limited to a relatively narrow range when compared to eclogitic diamonds. They contain inclusions of olivine ($Fo_{93–97}$), Mg-chromite, Cr-pyrope with high Mg#, enstatite, Cr-diopside, and Ni-rich monosulphide solid solution (see Stachel and Harris, 2008 for a review). The compositional range reported for the specific parageneses of peridotitic inclusions varies from harzburgitic–dunitic through lherzolitic to wehrlitic. Yet, within any single "P-type" diamond, the chemistry of silicate inclusions of any particular species is almost identical, e.g., olivines in the same diamond will show little variation in Fo content. Chromites from single diamonds are the only exception and sometimes show a systematic variation in chemistry from inclusions located in the core towards those situated in the diamond rim (Bulanova, 1995; Sobolev and Yefimova, 1998). Peridotitic diamonds exhibit C isotope compositions consistent with the mean-mantle value, where $\delta^{13}C$ values range from −5 to −8‰ (see Cartigny, 2005 and Stachel et al., 2009) and individual crystals are typically limited to $\delta^{13}C$ variations within 4‰ (Navon, 1999). Additionally, oxygen isotope compositions of garnets from peridotitic diamondiferous xenoliths also exhibit compositions akin with that of the ambient upper mantle ($\delta^{18}O$ of 5.3 ± 0.6‰; Spetsius et al., 2008). Harzburgitic inclusions in diamonds typically yield Archaean ages of 2.8–3.5 Ga inferred by study of different radiogenic isotope systematics of silicate and sulphide inclusions (Richardson et al., 1984 1993; Pearson and Shirey, 1999; Gurney et al., 2010), whilst the lherzolitic group has younger Proterozoic ages (Richardson et al., 1993; Pearson et al., 1998; Gurney et al., 2010).

Conversely, eclogitic diamonds show a broader range of geochemical characteristics that imply formation within a wider variety of environments. Multiple inclusions of garnet and clinopyroxene from single eclogitic diamonds may record substantial compositional variation. For example, Sobolev et al. (1998a) reported large chemical variations for 35 garnet and 5 clinopyroxene inclusions within a single eclogitic diamond from the Mir pipe. Additionally, marked decreases of 25.5 to 14.4 for the Ca/Ca + Mg ratio of eclogitic garnets from core to rim located inclusions in an individual diamond from the Mir pipe were reported by Bulanova (1995) and Taylor et al. (1996, 1998). In comparison to peridotitic diamonds, eclogitic samples also record a larger range of $\delta^{13}C$ values from +5 to −41‰ (e.g., Cartigny, 2005 and references therein; De Stefano et al., 2009). Carbon isotope variation within single eclogitic diamonds can exceed 10‰ (Bulanova et al., 1998; Fitzsimons et al., 1999; Hauri et al., 2002; Schulze et al., 2004; Wiggers de Vries et al., 2007; Mikhail et al., 2014b). Furthermore, garnets from eclogitic diamondiferous xenoliths record a wide range of values of $\delta^{18}O$ from +4.7 to +9.7‰ (Spetsius et al., 2009). Additionally, dating of eclogitic diamond inclusions has provided evidence of their formation in distinct episodes over a wide range of geological time from 2.9 to 1.9 Ga (Richardson et al., 1990, 2001; Smith et al., 1991; Pearson et al., 1998; Aulbach et al., 2009; Shirey and Richardson, 2011). Therefore eclogitic diamonds appear to form under variable conditions and from variable sources, in contrast to their peridotitic counterparts.

Cathodoluminescence (CL) imaging typically reveals simple octahedral internal growth zonation for both peridotitic and eclogitic diamonds; complicated zonation is rarer. Seventy per cent of a collection of several thousands of Yakutian diamonds display simple octahedral growth zonation with only 30% recording complex histories where the crystal habit changes during growth (Bulanova, 1995). Within the cores of diamonds several crystal habits can exist (cubo-octahedrons, cubes, aggregates or broken crystals) that were overgrown by later octahedral layers (Seal, 1966; Tolansky, 1966; Varshavsky, 1968; Frank, 1969; Genshaft et al., 1977; Lang, 1979; Bescrovanov, 1992; Bulanova et al., 1993). Diamonds from kimberlites also exhibit internal and external features of resorption and etching. The final stage of external diamond resorption is generally regarded as taking place during upward transportation in kimberlite magma (Orlov, 1977; Robinson, 1978; Robinson et al., 1989), but individual crystals have complicated histories of early stages of resorption, etching, fracturing, breakage and new stages of re-growth. These diamonds with complex growth histories provide unambiguous evidence of changing fluid–melt activity and stress in the mantle and represent a valuable record of evolving geological conditions during diamond formation, mantle residence, metasomatism in the sub-continental mantle and finally, their transportation towards the crust.

Several fundamental unresolved questions remain about diamond genesis. Is there any age difference between the eclogitic diamonds with enriched and depleted ^{13}C values? What is the degree of mixing, and the proportions involved, between mantle- and crustal-derived carbon (and nitrogen) during eclogitic diamond-formation?

Here we investigate an eclogitic diamond from Mir kimberlite, Yakutia, which exhibits variable $\delta^{13}C$ values across concentric growth zones. These zones show both ^{13}C-depleted and mean-mantle $\delta^{13}C$ values. In addition, the sample contains mineral inclusions indicating a sharp change in mineral composition and in pressure–temperature (P–T) parameters during formation. The aim of our study is to reconstruct the conditions of diamond growth, to explain what processes caused the sharp changes in the internal structure, isotope composition and chemistry of the inclusions, and to show how these variations relate to the origin of eclogitic diamonds in general. The results of our study are compared with published data on eclogitic diamonds from the Mir pipe and on a global scale.

2. Geological setting and sample description

The 360 Ma aged Mir pipe kimberlite (Kinny et al., 1997) intrudes Cambro-Ordovician terrigenous sediments, carbonates, evaporites and late Devonian diabases. The crystalline basement rocks are biotite–amphibole tonalite–trondjemite gneisses, granite–gneisses and granites with Nd model ages ~3.3 to 2.6 Ga (Smelov et al., 1998; Kovach et al., 2000) that form part of the Archaean granite–greenstone complexes of the Tunguska Terrain (Fig. 1). The neighbouring basement of the North-Asian Craton, including the Siberian platform (Fig. 1), is formed of Archaean and Palaeoproterozoic terrains (Rosen and Turkina, 2007; Smelov and Timofeev, 2007). Collision of these terrains between 1.99 and 1.86 Ga resulted in the formation of the Siberian platform basement (Rosen and Turkina, 2007). Basalt andesite–rhyolitic paragneiss and intrusive complexes of granulite and amphibolite facies occurring to the East of the Tunguska Terrain were formed on the active continental margins between 2.4 and 1.98 Ga (Velikoslavinskii et al., 2006; Smelov et al., 2012). At approximately the same time, the Bilyakh–Fedorovskaya subduction zone was active beneath the Tunguska Terrain (Fig. 1) explaining the presence of eclogite and diamonds with ^{13}C-depletion in the mantle lithosphere that were later sampled by the Mir kimberlite. The existence of the Mesoproterozoic Nyurba rift to the South of Mir pipe was identified by deep drilling, where basic rocks (gabbro-diabases and diabases) were found at a depth of 2.7–3.3 km. These Proterozoic basic rocks (~1.2 Ga $T_{Nd}DM$ model-age) have compositions comparable to ocean island basalts (Kovach et al., 2000).

Diamond 1703 from the Mir kimberlite is a 5 mm colourless octahedron elongated along a symmetry axis of the second order (L_2), having several inclusions of silicates and sulphides surrounded by rosettes of black local cracks. All inclusions have octahedral diamond-imposed