

Origins of diamond forming fluids – constraints from a coupled Sr-Nd isotope and trace element approach.

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1. Introduction

Sub-micrometer inclusions in diamonds carry high-density fluids (HDF) from which the diamonds have precipitated. HDFs bearing microinclusions are common in fibrous growth zones in cubic diamonds as well as in cubic growth zones within octahedral diamonds.

The trapped HDFs are rich in volatile species (Navon et al., 1988) along with solutes varying between three end-members: (a) a silicic end-member rich in water, Si, Al, and K; (b) a carbonatitic end-member rich in carbonate, Mg, Ca and K and (c) a saline end-member rich in water, Cl and K (Schrauder and Navon, 1994; Izraeli et al., 2001).

All HDFs types display steep REE patterns with extreme enrichment in LREEs. They are rich in Pb and are depleted in Ti, Zr and Hf relative to primitive mantle (Schrauder et al., 1996; Zedgenizov et al., 2007). While trace element systematics have added to constraints on the origins of HDFs, radiogenic isotopes potentially offer a powerful fingerprints of their source. Obtaining the radiogenic isotopic composition of diamond fluids has proven a challenging analytical task. Only two studies have so far presented such data. Akagi and Masuda, (1988) and Akagi (1999) analysed the Sr isotopic composition of HDFs trapped in fibrous diamonds and found $^{87}\text{Sr}/^{86}\text{Sr}$ ratios ranging between 0.70380 and 0.70516, similar to the range defined by Group I kimberlites (Nowell et al., 2004). Other radiogenic isotope systems were never analyzed.

The similarity of the early Sr isotope data combined with trace elements and the restricted normal mantle C isotope compositions of the host diamond supported a

strong link between HDFs and kimberlites (Boyd and Pillinger, 1994; Schrauder and Navon, 1994; Klein-BenDavid et al., 2007; Zedgenizov et al., 2007). Nevertheless, the link to kimberlites is not supported by other observations, e.g. Kimberlites carry higher silica and lower potassium and volatile contents than diamond forming fluids. Various mechanisms, such as metasomatic interaction of fluids with mantle rocks, melting of carbonated mantle or fractional crystallization and immiscible separation of kimberlitic melts have been proposed as the mechanism for the evolution of the parental fluids.

Here we present the first ever coupled Sr, Nd and Pb isotope ratios and trace element abundances of HDFs in fibrous and coated diamonds from Africa, Canada, Russia and Guinea. We also report C isotopes measured from some of the host diamonds.

2. Methods:

Diamonds were laser ablated using a custom made sealed Teflon cell with a laser window. The ablation products were collected in dilute HCl and dried down. The dried sample was dissolved in dilute HNO₃. 10% of the sample was aliquoted for trace element analysis. The remaining sample was passed through micro-Sr columns to separate the Sr and Pb fractions. Nd was purified using an additional cation column. Trace element analyses were performed on an Element II ICP-MS. Sr isotope compositions were measured by TIMS (Triton) while Pb and Nd isotope ratios were measured by MC-ICP-MS (Neptune).

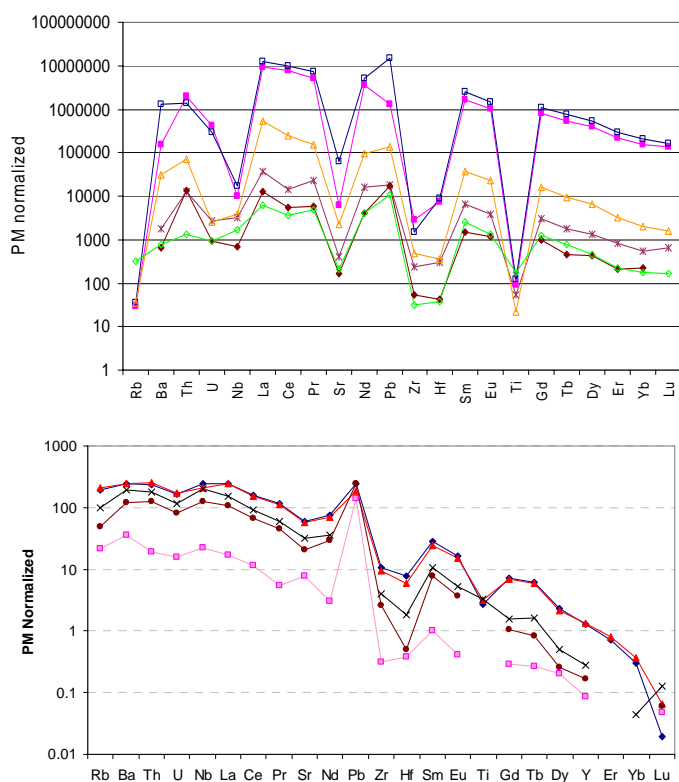


Figure 1: Primitive mantle normalized trace element patterns of HDFs: top - diamonds from Botswana; Bottom – Udachnaya, Siberia. Abundances calculated from diamond weight ablated.

3. Results:

Thirty four diamonds from 7 different locations were analysed. All diamonds are enrich in LREEs, Pb and Th and are depleted in HFSE. Strontium behavior is variable. African diamonds display a deep negative Sr anomaly whereas those from Canada and Russia have almost negligible to small positive anomalies.

The Sr isotopic compositions span a wide range (0.70454 to 0.71817) between values similar to those of Group I kimberlites to highly radiogenic values well in excess of Group II kimberlites and more akin to some lamproites.

Fluids from Udachnaya diamonds have the least radiogenic Sr, and display similar values to those analyzed by Akagi and Masuda, (1988) for “Congo” stones. In contrast, some diamonds from Africa have highly enriched Sr isotope ratios. Five separate analyses were conducted on a single Botswanan diamond. A clear mixing relationship is evident between the five separate analyses, implying that diamond precipitation was linked to mixing of fluids with different Sr isotope compositions.

Individual Botswanan diamonds can be related to the same mixing curve, implying that fluid mixing is an important process in the precipitation of these fibrous diamonds. Other diamond suites also show similar indications of fluid mixing, e.g. for the Snap-Lake diamonds there is a positive correlation between Sr isotope composition and SiO_2 content (See Logvinova et al, 2008). For the Congo diamonds there is a positive correlation between the increase in the Th/U ratio and the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio.

Diamonds containing the highest density of fluid inclusions clearly have the highest trace element abundances and it is only these diamonds (that also had the most radiogenic Sr isotope compositions) that yielded sufficient Nd and Pb to permit isotopic analysis. The $^{207}\text{Pb}/^{204}\text{Pb}$ ratio of the analysed diamonds is highly radiogenic and plots significantly above the Northern Hemisphere reference line (NHRL), with $\Delta 207/204$ varying between 0.31 and 0.20. ϵ_{Nd} values are highly un-radiogenic (-16 to -41).

Carbon isotopes were analysed for all six diamonds from Botswana. $\delta^{13}\text{C}$ values all fall within the tight range of carbon isotopic compositions typical for fibrous diamonds (-5.4 to -6.8‰). This would imply that in a mixing scenario, either both end-members had similar C isotope compositions or one end-member had much more abundant carbon than the other and was able to dominate the carbon isotope composition of the resulting diamond.

4. Discussion:

The highly variable Sr isotopic compositions of the fibrous diamonds analysed here indicate that the diamond forming fluids within them are composed of two components: a highly radiogenic component that must have had a time integrated high Rb/Sr ratio and been isolated for a long time; and a less radiogenic component, probably from the convecting mantle, that is similar in composition to kimberlite and carbonatites.

The un-radiogenic Sr end-member: We suggest that the major element compositional range of HDF is the outcome of mineral fractionation and fluid immiscibility of primary carbonatitic fluids that are closely related to the proto-kimberlite in the mantle (Klein Ben-David et

al. 2007). The composition of a proto-kimberlite at depth may be significantly different from that observed on the surface. Similar MgO, CaO and FeO contents between diamond forming fluids and kimberlites from Udachnaya have been recently reported (Klein-BenDavid et al., under revision). These diamonds also have the least radiogenic Sr isotopic compositions that are similar to kimberlite. However, a persistent problem is the low alkali content of kimberlites (Kjarsgaard et al, 2008 – this volume) compared with the extreme alkali enrichment in the HDFs. Evolution of this single component via fractional crystallization to lower alkali contents can not explain the observed Sr isotopic range in the HDFs. For this reason, another fluid component is required, as indicated by the Sr isotope mixing relationships.

The radiogenic Sr end-member: The very elevated Sr isotope compositions of some of the diamond HDFs, together with their elevated $^{207}\text{Pb}/^{204}\text{Pb}$ ratios and very low ϵNd values require long-term evolution in an ancient reservoir such as the lithospheric mantle. Glimmerites are mica rich veins that are related to metasomatic enrichment in the lithospheric mantle. They have highly radiogenic Sr and un-radiogenic Nd isotopic signatures that span the range we see in fibrous diamonds and also have similar levels of LREE enrichment. In addition they are also rich in water and in some cases carbonate (Carlson and Irving, 1994; Becker et al., 1999). We suggest remobilization of such mica-rich veins as the source for the radiogenic Sr end-member observed in the diamond HDFs.

Fluid mixing: one of the main components in fibrous diamond growing fluids is carbonate. Diamond precipitation occurs in an environment where both carbonate and diamond can remain stable. Such conditions are limited to the vicinity of the EMOD buffer. Fluids that are related to low fraction mantle melts originate from the asthenosphere and are probably of a relatively reducing nature, while fluids extracted from mica rich veins are water-rich and may be more oxidizing. We suggest that the mixing of these fluids moves the system towards the EMOD buffer and hence enhances diamond precipitation.

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