Tracing diamond genesis and provenance: Sr-Nd isotope and trace element compositions of fibrous diamonds from the Congo and application to gem quality samples

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Overview and methodology

Fluid-bearing micro-inclusions in diamonds provide a unique source of information on the diamond crystallization environment. The composition of a diamond forming fluid is an integrated function of its source components and should record the fluid-rock interactions and mixing processes experienced by the fluid, prior to and during diamond crystallization. Documenting the isotopic and trace element characteristics of the fluids trapped within fibrous diamonds thus provides powerful genetic information, especially relating to the time-integrated history of the fluid source regions.

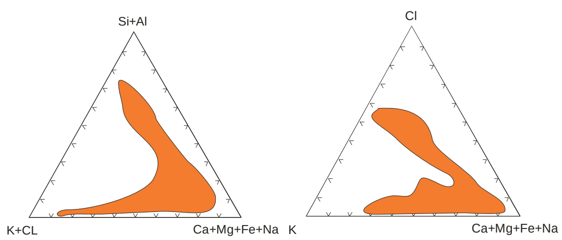

Figure 1. Compositions of microinclusions from worldwide localities. Hydrous silicic melt endmember composition falls close to the Si+Al apex. The carbonatitic melt falls close to the Ca+Mg+Fe+Na apex and the K+Cl represents the brine.

The compositions of diamond-forming fluids fall along two continuous arrays: 1] Between a carbonititic end-member diamond rich in carbonate, CaO, FeO, MgO, Na_2O, K_2O and BaO and a silicic end-member rich in water, SiO_2, Al_2O_3 and K_2O; 2] An array defined by a carbonititic end-member and a saline end-member rich in K, Cl and water. (Izraeli et al., 2001; Klein-BenDavid et al., 2006a,b). These fluids have steep REE patterns with the LREE's displaying moderate enrichment (Akagi & Masuda, 1986; Schrauder et al., 1996; Rege et al., 2003 & 2005; Zedgenizov et al., 2007). Zr, Ti, Sr, Pb and Nb show negative anomalies with low Sm/Nd ratios that have the potential to develope extreme Sr and Nd isotopic compositions. These patterns resemble those of carbonatites and kimberlites. They are also rich

Figure 2. Surface photomicrograph of a polished section of CTPb2 - a coated stone with octahedral core and fibrous coat. The transparent inclusion-poor core (with minor feathers and internal dislocations) is surrounded by a series of fluid-rich zones of high inclusion-density. Photograph by O. Klein-BenDavid.

in P, K and water, sharing these features with glimmerites.

We have developed a new technique that allows, for the first time, acquisition of trace element concentrations, Sr and in some cases Nd+Pb isotope compositions of diamond-forming fluids. Furthermore, our method allows high quality trace element data to be obtained on high purity gem quality diamonds.

Here we present combined Nd-Sr isotopic data and trace element compositions for fluids trapped within five fibrous and coated 'Congo top' diamonds. These samples have cubo-octahedral form and have been halved on their shorter x-y axis. Their individual weight ranges from 19 to 29mg.

Physical sampling techniques are based around a computer controlled New Wave Nd: YAG 213 nm UV laser ablation system. Despite being time consuming, the off-line ablation and chemical separation allow the most versatility in pre-concentrating analyte levels and optimizing measurement approaches to yield the best quality data for both trace element and isotopic

Figure 3. Diamond CNG-23 enlarged showing post-ablation raster pattern.

measurements. Concentration data is reported relative to the mass of diamond ablated.

Results and discussion

Clean diamonds are mounted in a specially engineered laser cell and held in place under their own weight. On average the samples lose 0.3mg in weight during analysis. The ejecta is taken up in acid, aliquoted for trace elements and run through columns to collect the matrix elements for mass spectrometry.

On multi-element plots all of the Congo fibrous diamonds show broadly similar inter-element fractionation patterns. Different zones within the same diamond also yield similar inter-element fractionation. All five diamonds show negative Nb_{pm}, Sr_{pm}, and Ti_{pm} anomalies and positive Th_{pm}, La_{pm} and Pb_{pm} anomalies. Zr_{pm} and Hf_{pm} are low (Fig. 4). These features are common to diamond-forming fluids from other locations (Klein-Bendavid, *this volume*). In all analyzed diamonds Sr/Yb and Zr/Yb are positively correlated, indicating coupled enrichment of both LILE and HFSE. Both La/Yb and Nd/Ba show strong positive correlation with $^{87}Sr/^{86}Sr$, i.e. enrichment of LREE's with increasing radiogenic Sr.

In contrast to previous Sr-isotope measurements of Congo fibrous diamonds, e.g. $^{87}Sr/^{86}Sr$ = 0.70360 to 0.70516 (Akagi and Matsuda, 1998; Akagi, 1999) the measured Sr isotope compositions of Congo diamonds in this study show enormous variation ($^{87}Sr/^{86}Sr$ = 0.72335 to 0.70673). The sample displaying the most radiogenic $^{87}Sr/^{86}Sr$ has an extremely low ε_{Nd} value (-41.6). The extreme Sr and Nd isotopic compositions indicate long-term (>Gyr) evolution of one of the fluid components. Comparisons with fibrous diamonds from other localities worldwide indicate that their highly radiogenic Sr is usually accompanied by very unradiogenic ε_{Nd} (Klein-Bendavid, *this volume*).

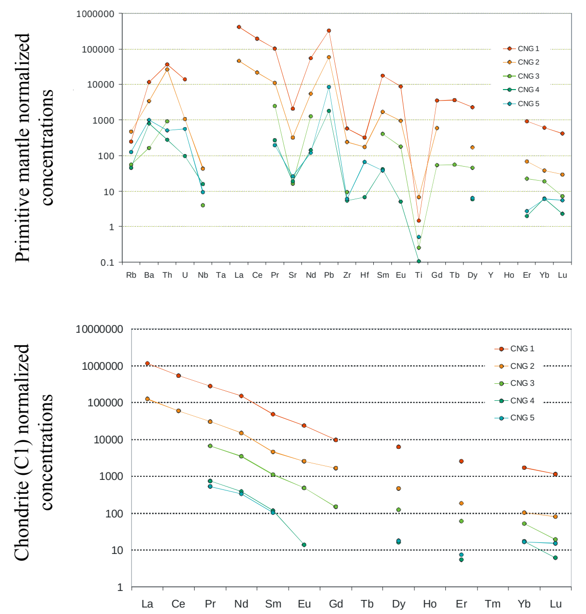

Figure 4. Elemental concentrations of 5 fibrous and coated 'Congo-Tops' diamonds. REE patterns are steep and reproducible, forming parallel arrays that are again similar to fibrous diamond trace element patterns from other locations. (Klein-BenDavid; *unplublished data*)

Previous work by Zedgenizov et al, 2007 and Klein-BenDavid et al, 2006b, suggest that trace element systematics and carbon isotopes display a convecting mantle signature for the diamond-forming fluid source. Highly radiogenic Sr and very unradiogenic Nd (very –ve ε_{Nd}) isotope compositions are not consistent with this simple picture and instead indicate the additional involvement of an old enriched continental lithospheric endmember. To account for these observations we propose a model where fibrous diamonds form via a mixing process between two fluid/melt components:

1) A fluid that has very radiogenic Sr with unradiogenic Nd, highly enriched in most trace elements, that probably originates from within the continental lithosphere and,

2) A fluid/melt that has Nd-Sr isotopic characteristics more akin to the convecting mantle, possibly kimberlite or carbonatite.

Future work on 'gem-fingerprinting'

Trace element analysis on a gem diamond from Udachnaya, Siberia displays a multi-element pattern similar to more inclusion-rich fibrous samples from worldwide sources and has yielded concentrations several orders of magnitude above our method detection limits. In contrast, incompatible trace element abundances in most gem diamonds are close to, or below the method detection limits of direct laser ablation techniques, e.g. Rege et al, 2005 (Fig. 5).

Concentration in Fibrous / Gem diamonds compared with method detection limits – A comparison between 'off-line' and 'direct' laser ablation techniques

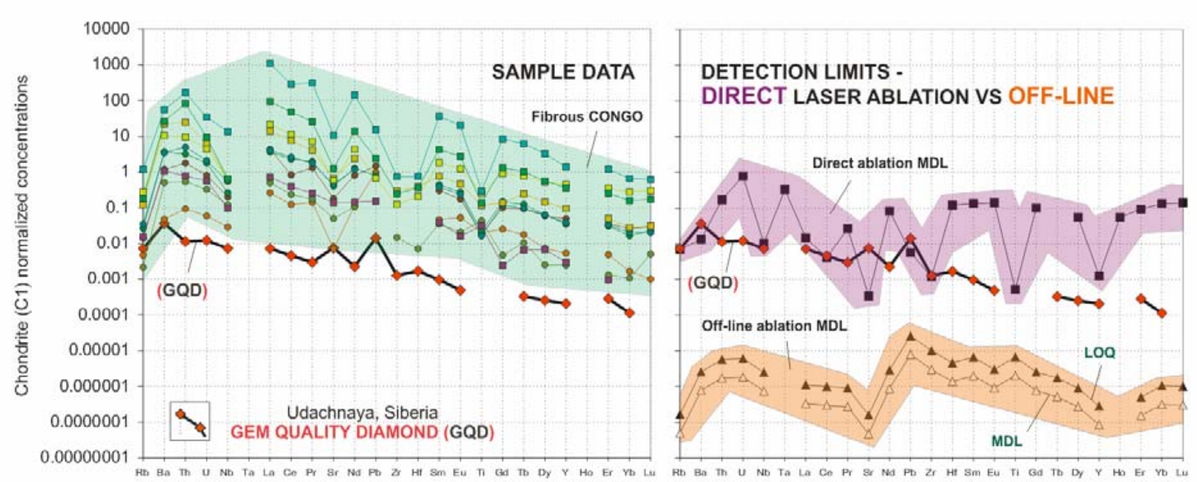

Figure 5. OFF-LINE Ablation [LEFT] - Fibrous inclusion-rich 'Congo-Tops' along with a high purity gem quality diamond from Udachnaya. (John McNeill; *unpublished data*). DETECTION LIMITS COMPARISON [RIGHT] – Method detection limits for off-line ablation shown by orange area. LOD - Limit of Detection ($3*SD_{TPB}$); LOQ - Limit of Quantification ($10*SD_{TPB}$) (John McNeill; *unpublished data*). MDL for direct ablation in light purple from Rege et al, 2005.

In the future we will focus on obtaining high-quality trace element and possibly Sr isotope data on gem-diamonds. This will allow a more rigourous assessment of the geochemistry of diamond-forming fluids from different parageneses and may enable further advances in 'fingerprinting' distinct diamond populations.

Combined Sr isotope and trace element patterns offer some promise in this regard and Botswana, Congo and Snap-Lake fibrous diamonds can be distinguished on this basis. Therefore in its simplest form, when extended to gem diamonds this information could potentially be used to determine the source of commercial stones whose country of origin is under question.

Acknowledgments:

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