Origins of Diamond-forming Fluids from the Slave Craton: Trace Element Constraints on a Variety of Diamonds from the Ekati Mine

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Summary
Diamonds from a single kimberlite often show a wide variation in growth morphology and mechanism (e.g., fibrous versus smooth faced octahedral crystalline). This variability, along with a wide spectrum of nitrogen aggregation systematics indicate the presence of several generations of diamonds at a single mine, raising the possibility of a variety of origins. Here we present trace element data for fluids trapped within a suite of twenty-three diamonds from the Ekati property, N.W.T, previously characterized by Gurney et al. (2004), to investigate the potential variation in parental, diamond-forming fluids from a single mantle section of the Slave craton. This suite forms a part of a much larger study on Slave diamonds in general.

Evidence of at least two types of diamond-forming fluids within gem diamonds is observed. One group has enrichments in LILE over Nb (which is also displayed in the fibrous diamonds), whereas a second group has normalized LILE abundances more similar to Nb. These two groups bear some similarity to different groups of fluid-rich diamonds from other locations, providing some supporting evidence of a link between the parental fluids for both fluid-inclusion-rich and gem diamonds. Isotopic information further supports a model of either several mantle components being involved in the formulation of a diamond-forming fluid, or different fluids being present in the same section of Slave craton resulting in diamond populations with differing chemical signatures.

Introduction
Perhaps the most important information required to understand the origin of diamonds is the nature of the fluid that they crystallize from. Progress in constraining the identity of the diamond-forming fluid for high purity gem diamonds that contain very low concentrations of fluid inclusions has been hampered by analytical challenges. In contrast, significant recent advances have been made in the understanding of fluids that are parental to fibrous diamonds. Early studies of the major element composition of fibrous, fluid-rich diamonds recognized the K-rich nature of the entrapped fluids and suggested a link to kimberlitic magmatism (Navon et al., 1988). Subsequent studies of the trace element systematics of these fluid-inclusion-rich diamonds using either INAA (Schrauder et al., 1996) or LA-ICPMS (e.g. Weiss et al., 2008) have supported this early conclusion, with some studies invoking carbonatite instead of kimberlite as a parental fluid. This study uses a new technique to acquire trace element and isotopic information on a variety of Ekati diamonds in order to further support and constrain the origin of diamond-forming fluids of the Slave craton. All samples are from the Fox and Misery pipes on the Ekati property. The suite consists of two black fibrous cubes, one non-fibrous cube with a grey skin, one colourless non-fibrous cube, one colourless coated octahedral diamond and nineteen gem monocrystalline octahedral and dodecahedral diamonds including two gem fragments ranging from colourless to yellow and brown.
Method
This study was undertaken using a new ultra-low level method for the quantitative analysis of fluid-poor gem diamonds (McNeill et al., 2009). The method employs a closed-system laser ablation cell, where diamonds are ablated, with the products being trapped for later pre-concentration into solutions that are analyzed by sector-field ICPMS. Repeatibility of blanks yielded consistently low values so that for the elements Rb, Y, Nb, La, Pr, Eu, Gd, Tb, Dy, Er, Lu, Hf, Th & U, our Limits of Quantitation (LOQ) is less than 1 pg and in some cases, e.g., U << 1 pg (0.037 pg). Ce, Nd, Sm and Yb are all less than 3 pg, while for Sr the LOQ is < 10 pg. After a 5hr ablation on each of these Ekati diamonds enough Sr was concentrated (>0.5ng) from each of three stones to measure Sr for isotopes (TIMMS) in addition to trace-element profiles. Two of these diamonds are cubes of the fibrous growth form and the third a coated octahedral diamond.

Results and Discussion
The cubes and coated stone have relatively higher concentrations for a wide range of elements (expressed by weight in the solid) when compared to the gem stones. The former have rare earth elements ranging from 0.2 ppb - 6 ppm along with Y, Nb, Cs. Large ion lithophile elements (LILE) such as Rb and Ba vary from 2 ppb – 180 ppm. The gems’ REEs range from 0.1 ppt – 30 ppb while Rb, Sr and Zr are all in the range 0.2 ppb – 0.4 ppm.

Trace element patterns of this Ekati diamond suite show enrichment of the LREE compared to the HREE. Abundances decrease with increasing elemental compatibility. REE patterns are steep and reproducible, forming parallel arrays that are similar to fibrous diamond trace element patterns from other locations.

Primitive mantle normalized multi-element data reveals the presence of two general types of diamond-forming fluids within the gem diamonds. One group displays enrichments in large ion lithophile elements (LILE:- Ba, U, La) over Nb. Fibrous diamonds analysed in this study match this first display. The other has normalized LILE abundances more similar to Nb. Other than these differences diamonds of both the fibrous and monocrystalline growth form show broadly similar elemental systematics focused on strongly positive Pbpm, and Sfpm, negative Cemp, and Zrpm and Hfpm, that are low and flat. One deviation from these trends appears in a group of five diamonds from one location that have a positive Nbpm anomaly.

These two groups bear some similarity to different groups of fluids observed in fluid-inclusion-rich diamonds (Weiss et al., 2008), providing some supporting evidence for a link between the parental fluids for both fluid-rich and gem diamonds suggested from silicate inclusion chemistry (Tomlinson et al., 2009). We do not see the ‘table and bench’ relationship observed from other locations e.g. Weiss et al. 2008, 2009; Klein-BenDavid et al., 2010, and as seen in our data from Congo stones from another study. As a suite these diamonds show much less inter-element fractionation. At this stage the pipe from which the diamonds were extracted, Fox and Misery, cannot be distinguished based on trace-element chemistry. This may simply be due to the small sample set or to the broad range of diamond characteristics within the sample set.

Concentrations of La, Th, Ba and Nb show strong positive correlation over 4 orders of magnitude. The variations in concentrations for fibrous stones are a function of inclusion density. The concentrations of HREEs are much lower for all diamonds and there is substantial overlap between fibrous and gem samples. La/Th and La/Nb ratios for the majority of diamonds are close to 1, but vary between 10 and 0.1. More variable La/Yb and Nd/Hf ratios may be associated with the influence of solid micro-inclusions contained within the ablated material, or with depletion in the fluid of certain elements remaining behind in partially dissolved mantle minerals from which the original diamond forming fluid has been partly derived.
When plotted with average whole rock kimberlite and carbonatite from worldwide sources, multi-element systematics for cubes and fibrous diamonds from Ekati resemble kimberlite especially, deviating significantly only in negative Nb$_{pm}$, positive Sr$_{pm}$ and the total elemental concentrations, which are lower than whole rock kimberlite by 3 orders of magnitude. The similarity is not so apparent with gem diamonds. The measured Sr isotope compositions of three diamonds from the Fox pipe show large variation from a depleted and unradiogenic end-member within the OIB range to much more radiogenic values similar to lamproites and GP II kimberlites. These ratios are within the range seen by other authors (Klein-BenDavid et al., 2010). Multi-element plots however are very similar between these diamonds. These observations support the idea of either several mantle components being involved in the formulation of a diamond-forming fluid, or different fluids being present in the same section of Slave craton.

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References