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THE CONTRAST IN TRACE ELEMENT CHEMISTRY AND VOLATILE COMPOSITION BETWEEN FLUID INCLUSIONS IN FIBROUS AND OCTAHEDRAL DIAMONDS

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INTRODUCTION

Studies of fluid inclusions in diamonds have been limited by several factors. One factor is that studies have focused on fibrous diamonds, because they contain abundant fluid inclusions. Octahedral diamonds almost never host fluid inclusions, at least that are documented easily. Here the term "octahedral" is used here to refer to genesis by non-fibrous, facetted {111} growth, not necessarily the eventual morphology.

A second limitation is that the fibrous diamonds studied are relatively young compared to the majority of octahedral diamonds. These two factors mean that our knowledge of fluid equilibrated with diamond is limited to young, fibrous diamond-forming fluids. This study focuses on two unique diamond suites to address these issues: Archean fibrous diamonds and fluid inclusion-bearing octahedral diamonds.

SAMPLES

Two diamond suites were studied. The first consists of 6 translucent, grey fibrous diamonds recovered from an Archean metaconglomerate in the Michipicoten Greenstone Belt of the Wawa subprovince, Canada. Three diamonds are fibrous coatings over octahedral cores, while the other three are fibrous cuboids. The diamonds were originally emplaced by a kimberlite into a >2.7 Ga nucleus of the Superior craton (Kopylova et al., 2011). The Wawa fibrous diamonds are unique because they are close in age to, or slightly older than, their ~2.7 Ga host. Thus, the contained fluid inclusions may be the oldest mantle fluids available for study.

Fluid inclusion compositions are saline—carbonatitic, based on electron microprobe analysis. The sub-micron-size fluid inclusions contain crystallized solid daughter phases and residual fluid. Daughter minerals in the Wawa diamonds include sylvite, halite, dolomite, and Ca-Mg-Fe- Ba carbonates, revealed by X-ray diffraction (Smith et al., 2011). The fluid inclusions coexist with P-type mineral micro-inclusions like olivine and Cr-pyrope, indicating a harzburgitic diamond origin.

The second suite consists of 5 non-fibrous, octahedral, alluvial diamonds from the Northeastern Siberian Platform. The diamonds are rounded, equant to elongate octahedra with an overall yellow-orange or grey colour, and mechanical abrasion suggestive of a Precambrian primary source (Afanas'ev et al., 2009). Their fluid inclusions are 1—40 µm across, colourless, monophasic, and nearly flat, with polygonal boundaries. They lie along healed fractures in the diamond. The fluid inclusions are secondary, but originate from the diamond stability field, as the hosting fractures within the diamonds are healed. Rutile, coesite, and kyanite are found as inclusions with imposed diamond morphology as well as along fractures, consistent with an eclogititc paragenesis.

METHODS

The Wawa fibrous diamonds were analyzed by infrared spectroscopy to gauge bulk fluid inclusion volatiles not represented in electron microprobe analysis. Infrared spectroscopy was carried out at the University of Alberta, Canada.

Raman spectroscopy was used to measure compositions of fluid inclusions in the Siberian, octahedral diamonds. Spectra were measured at Durham University, UK, using a 532 nm green laser and 1800 g/mm grating. The Siberian diamond fluid inclusions were also examined by microthermometry in the range of -180—20 °C using a heating/cooling stage at the University of British Columbia, Canada.

Trace element and Sr isotope measurements followed the methodology described by McNeill et al. (2009) and Klein-BenDavid et al. (2010), employing off-line laser ablation to accumulate a sample in a closed system. Samples were collected and analyzed at Durham University, UK.

RESULTS AND DISCUSSION

Volatile Components

Infrared spectroscopy of the Wawa, fibrous diamonds shows water as the primary volatile. An average concentration (bulk diamond) of ~100 ppm was calculated from peak height at 3400 cm-1 (Weiss et al., 2010). All spectra show carbonate peaks, from carbonate daughter minerals that have crystallized from the fluid. Small CO2 peaks were also found in two diamonds. Nitrogen is poorly aggregated in all the fibrous diamonds, indicating that the diamonds were essentially contemporaneous with volcanic sampling/ transport.

Raman spectra of the fluid inclusions in Siberian, octahedral diamonds reveal CO2 and N2. Estimated molar proportions of N2/(CO2+N2) are within 0.2—0.8, based on peak areas (Burke, 2001). This composition agrees with results from Tomilenko et al. (1997) for diamonds from the same NE Siberian placer. Diamond peaks are shifted upward by 0.6 cm-1 near the inclusions, corresponding to a ~0.3 GPa local pressure increase (Grimsditch et al., 1978), which can be taken as a minimum pressure in the fluid inclusions. More importantly, fracture healing and polygonal inclusion boundaries point to fluid trapping within the diamond stability field. Elastic deformation of the inclusion walls likely relieves some fluid inclusion pressure due to their flat and irregular shapes (Burnley and Davis, 2004).

Upon warming in the range -180—20°C the fluid inclusions show either no changes, or exhibit melting of a single solid CO2 phase (Figure 1). This behaviour is consistent with higher fluid densities than those of crustal fluid inclusions (Van

Figure 1. Example of spontaneous nucleation of solid CO2 upon cooling. The solids appear as multiple rounded blobs that are brighter than the surrounding fluid. The solids quickly reorganized into two discrete blobs comprising ~40% of the inclusion volume. Upon subsequent heating, final melting occurred at -63 °C.

den Kerkhof and Thiéry, 2001). Solids occupy 30—90% of the inclusion volume at the maximum extent of solidification.

A strong contrast is evident between the fluid inclusions in Wawa fibrous diamonds and the Siberian octahedral diamonds. The Wawa fluid is a volatile-rich saline— carbonatitic melt, with water being the dominant volatile. Fibrous diamond fluid inclusions typically contain 10—25% water (Weiss et al., 2010) and only minor amounts of CO2, as most of the carbon is present as carbonate (Navon et al., 1988).

However, the Siberian octahedral diamonds contain fluid inclusions that are totally volatile, CO2 and N2 mixtures. Small amounts of graphite and other minute solids may accompany the fluids in healed fractures, but these fluid inclusions contain nothing like the daughter minerals that dominate fibrous diamond fluid inclusions.

TRACE ELEMENTS

Chondrite normalised trace element patterns for all samples are shown in Figure 2. The octahedral, Siberian diamond fluids exhibit similar patterns across all 5 diamonds, with elevated Un, Zrn, and Hfn. The octahedral diamond fluids are distinct from the fibrous, Wawa diamond fluids. The Wawa samples can be divided into two groups, most easily distinguished by contrasting Thn/Un ratios. Interestingly, the high Thn/Un group corresponds to fibrous diamond coats (W1, W1(A2), W7, W9) and the low Thn/Un group corresponds to fibrous cuboids (W14, W29, W50).

The octahedral diamond fluids have generally flat REE patterns (Lan/Ybn = 0.5—7), with either mild LREE enrichment or mild HREE enrichment and weak negative Eu anomalies. The elevated HREE and low Lan/Ybn of the Siberian fluids suggests that garnet breaks down to contribute to the fluid.

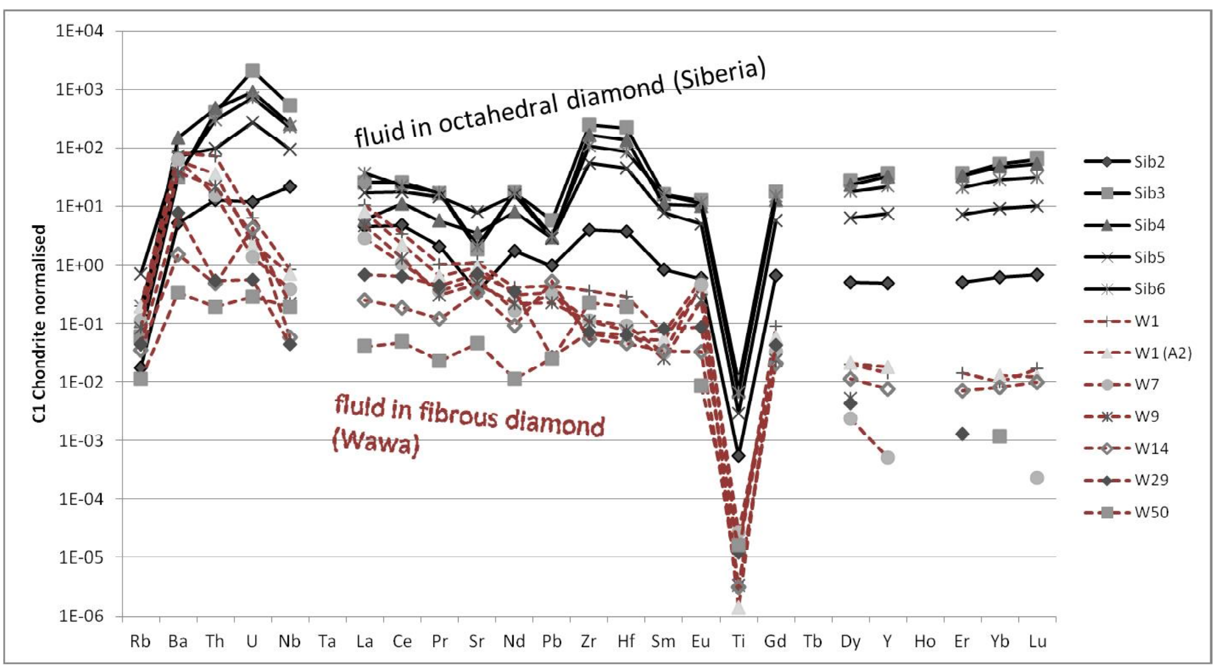

Figure 2. Trace element data, normalised to C1 chondrite (McDonough and Sun, 1995) and the diamond mass difference before and after ablation.

In contrast, the Wawa fibrous diamond fluids have steeply-sloping patterns (Lan/Ybn = 30—1000). The high Lan/Ybn indicates residual garnet control, as in small degree alkalic melts from lherzolites. Fibrous coat samples (W1, W1(A2), W7, W9) have pronounced positive Eu anomalies (Eu/Eu* = 1.8—3.5) compared to fibrous cuboid samples, as well as stronger LREE enrichment. Positive Eu anomalies may suggest original derivation of the fluid from shallow, plagioclase-bearing depths.

A comparison with other diamond fluid inclusion trace element patterns from the literature is given in Figure 3. The fibrous, Wawa diamonds correspond somewhat to the "table" category of pattern shapes defined by Weiss et al. (2009), based on high Ban, Thn, Un, and Lan compared to Nbn. Such patterns are characterized by high degrees of inter-element fractionation, particularly between HFSE and LILE. However, the Wawa fluids differ from the "table" category by having notably higher Srn/Ndn, Zrn/Smn, and Hfn/Smn.

A closer match to Wawa fibrous diamond fluids is offered by fibrous diamond fluids from the Panda kimberlite, Ekati mine, NWT (Figure 4) (Tomlinson et al., 2009), whose saline—carbonatitic fluid compositions also resemble those from Wawa (Tomlinson et al., 2006). Both the Wawa and Panda fluids have Srn/Ndn>1, a feature that has only been observed in saline-type diamond fluid inclusions (McNeill, 2011).

The octahedral, Siberian diamond fluids do not bear strong resemblance to any group of diamond fluids analysed so far, in that they have relatively little primitive mantle normalised inter-element fractionations. The increasing sequence Rbn, Ban, Thn, to Un resembles the "fibrous low" patterns of Rege et al. (2010), but the octahedral, Siberian diamond fluids have anomalously high Zrn/Smn and Hfn/Smn, and do not exhibit the down-bowed LREE shape, negative Y anomaly, or low Zrn/Hfn ratio that characterize the "fibrous low" group (Figure 3). It is possible that this unusual trace element signature arises partly from minute solid inclusions that accompany fluids along the healed fractures, or from nano-inclusions in the surrounding diamond.

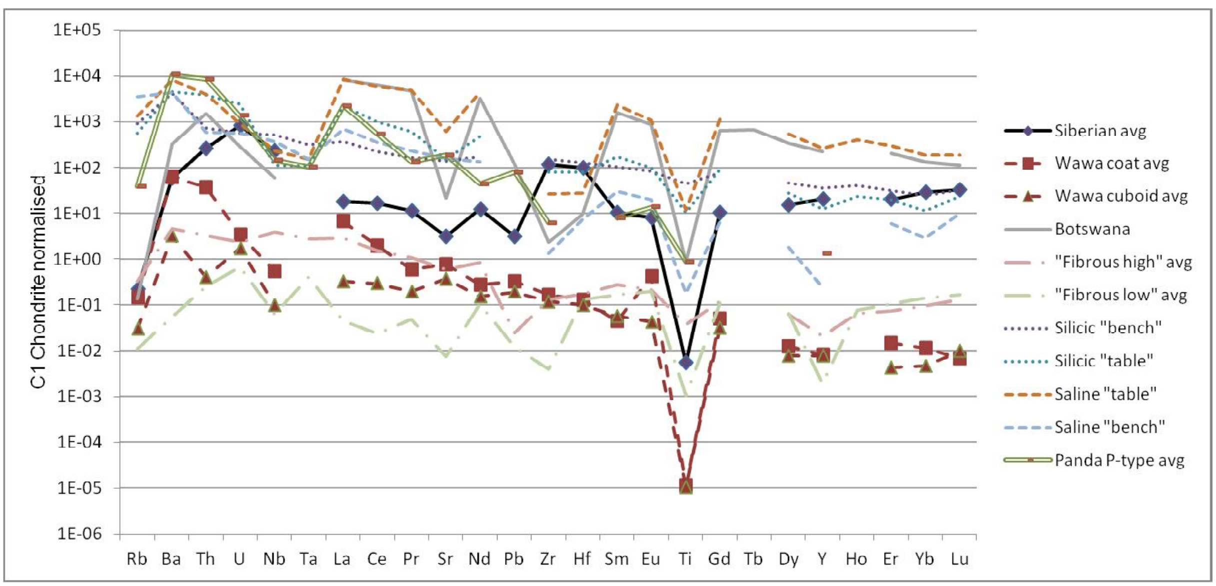

Figure 3. Trace element patterns of average octahedral, Siberian diamond fluid, average Wawa fibrous coat, and average Wawa fibrous cuboid compared to patterns from the literature. All values normalised to C1 chondrite (McDonough and Sun, 1995). Data sources: Botswana (Klein-BenDavid et al., 2010); fibrous high, fibrous low, bench and table patterns (Rege et al., 2010); Panda P-type (Tomlinson et al., 2009).

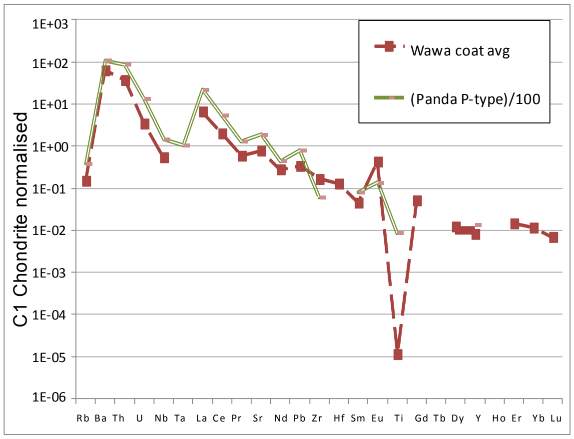

Figure 4. Comparison between the trace element pattern shapes of Wawa, fibrous diamond coats and an average of six P-type fibrous diamonds from the Panda kimberlite (Ekati) (Tomlinson et al., 2009). The Panda pattern is vertically shifted to aid in comparison.

Sr Isotopes

Wawa fibrous diamonds gave 87Sr/86Sr values of 0.7042—0.7078. Calculating initial 87Sr/86Sr using Rb/Sr ratios and an age of 2.7 Ga yields values of 0.699—0.702. Four samples have extremely low initial 87Sr/86Sr, approaching the Solar System initial of 0.69889, but also reflecting relatively large uncertainties in the measured Rb/Sr ratios due to low Rb contents.

Sr isotopes in the Wawa fibrous diamonds have a general positive correlation between Rb/Sr and 87Sr/86Sr ratios but they do not form a geologically reasonable isochron (i.e. greater than or equal to the 2.7 Ga deposition age of the Wawa metaconglomerate diamond host). This indicates that the fluids were isotopically heterogeneous, similar to findings from Botswana fibrous diamonds (Klein- BenDavid et al., 2010). While the uncertainties on the Rb/Sr ratios and resulting initial ratios are high, the low calculated $^{87}Sr/^{86}Sr_i$ ratios call for a source that experienced time-integrated depletion of Rb/Sr. This contrasts with the Botswanan fibrous diamond fluid sources (Klein-BenDavid et al., 2010), but is consistent with some Slave craton fibrous diamonds (Mc Neill, 2011).

Only one of the octahedral diamond samples contained sufficient Sr to allow $^{87}Sr/^{86}Sr$ measurement. Its very radiogenic $^{87}Sr/^{86}Sr$ value of 0.7130±2 is coupled with a Rb/Sr ratio that is too low to produce this radiogenic signature over any reasonable timescale. For example, an assumed age of 3 Ga gives a $^{87}Sr/^{86}Sr_i$ value of 0.709, well above bulk earth. Therefore, this Siberian, octahedral diamond has inherited a significant radiogenic Sr signature. This would require input from a high Rb/Sr phase that was isolated from the convecting mantle. Such an evolution has been observed for some gem diamond fluid sources from the Slave craton (McNeill, 2011).

Fluid Origins

The remarkable similarity of major and trace element composition between Wawa fibrous diamond fluid inclusions and saline-carbonatitic fibrous diamond fluids from the Ekati and Diavik mines in the Slave craton, Canada, suggests common fluid generating and growth mechanisms despite being in separate cratons and being separated by more than 2.5 Ga. Similar saline—carbonatitic fluid compositions are also present in some fibrous diamonds from the Kaapvaal and Siberian cratons (Izraeli et al., 2001; Zedgenizov et al., 2007). The Wawa fluid inclusions record direct evidence of Archean diamond growth from fluids of carbonatitic-character that are analogous to Phanerozoic examples. For the case of Wawa, Archean fibrous diamond genesis may also entail broader metasomatic processes, based on proposed genetic links between fibrous diamonds and kimberlites (e.g. Akagi and Masuda, 1988; Navon et al., 1988; Tomlinson et al., 2009; Weiss et al., 2011). A link to kimberlites is supported by Sr isotopes in the Wawa fluids, which are consistent with an asthenospheric origin.

In contrast, there are few examples of CO_2–N2 fluid inclusions from the mantle to draw in parallel with the Siberian, octahedral diamonds.

The closest match is olivine- hosted CO_2–N_2 fluid inclusions in spinel dunites from the Canary Islands (Andersen et. al., 1995). While the convecting mantle is one potential contributor for CO_2–N_2, the radiogenic Sr in the Siberian diamonds requires input from the sub-continental lithospheric mantle.

The anomalous levels of N in the Siberian fluids suggest either an efficient mechanism of N enrichment, or derivation from a N-rich source, such as subducted crust with organic N. A possible N-enrichment mechanism could be partial melting or recrystallization of NH4+ bearing clino-pyroxene (Watenphul et al., 2010) or other NH^+ bearing silicates. If NH_4^+ breaks down into N_2 and water, the water could be absorbed by surrounding minerals or partial melt, whereas N_2 may exsolve as a relatively insoluble supercritical fluid. Such a scenario may produce bubbles of N_2.

If CO_2 is present, it could scavenge N_2 to make a mixed fluid like the one trapped in the Siberian octahedral diamonds. One sign that mantle CO_2 could have an affinity to scavenge N_2 may be taken from the 13C/12C fractionation model proposed by Cartigny et al. (2001) for eclogitic diamonds. In this model, CO_2 escapes from a diamond-13 forming system, leaving it progressively depleted in C. Interestingly, the N content of eclogitic diamonds decreases systematically toward lower δ13C values, which could indicate that N_2 is scavenged by the escaping CO_2.

Aside from CO_2 and N_2, the Siberian fluid must have contained radiogenic initial Sr, likely inherited from a source with a high Rb/Sr phase. The high Rb/Sr requirement, coupled with high Zrn/Smn, Un/Thn, and Nbn/Lan could point towards the involvement of K-rich amphibole (Konzett et al., 1997; Moine et al., 2001). This would help explain the elevated Zr_n and Hf_n.

CONCLUSIONS

Fluid inclusions in the two studied diamond suites differ in both composition and trace element characteristics. The Archean fibrous diamonds from Wawa contain saline— carbonatitic fluids, whose trace element characteristics are similar to comparable Phanerozoic saline—carbonatitic fibrous diamonds. Initial 87Sr/86Sr ratios indicate that Wawa fluids are consistent with an asthenospheric source, while the Siberian fluids require contribution from a lithospheric source. The secondary fluid inclusions trapped in octahedral, Siberian diamonds are CO_2–N_2 mixtures, unlike the fluids found in fibrous diamond. Their unusual trace element systematics may reflect traces of solids trapped along fractures with fluid inclusions.

There seems to be a commonality between the fluids forming Wawa fibrous diamonds at 2.7 Ga and some much younger fibrous diamonds, implying similar diamond- forming processes.

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