VOLATILE - RICH BRINE AND MELT IN CANADIAN DIAMONDS

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INTRODUCTION

Mineral and fluid inclusions in diamonds provide us with a unique opportunity to investigate the mantle rocks where diamonds are formed and the fluids from which they crystallize. The fluid resides in micro-inclusions and spans a wide compositional range. Shcrauder and Navon (1994) found composition varying between silicate melts rich in Si, Al, K and H_2O and carbonatitic melts carrying large amounts of Mg, Ca, Fe and carbonate, in fibrous diamonds from Botswana. Izraeli et al. (2001) reported the finding of brine inclusions rich in Cl, K, Na and H_2O in diamonds from Koffiefontein. Mineral inclusions are rarely found together with fluid inclusions. Talnikova et al. (1995) reported the finding of omphacite along with silicic melt in a Siberian diamond and Izraeli et al. (2001, submitted) reported micro-inclusions of peridotitic and eclogitic minerals along with brine inclusions in cloudy diamonds from Kofeifontien.

Here we report the composition of five hundred micro-inclusions in twelve diamonds from the Diavik mine (Canada). The inclusions carry brine, carbonatitic melts and intermediate compositions between the silicic and carbonatitic end members. They also carry peridotitic minerals.

As all the diamonds come from a single mine, the occurrence of all three types of fluid provides us with a powerful tool for investigating their chemical evolution and their relation to the diamond growth.

METHODS

Eleven of the twelve Diavik diamonds we analyzed have an octahedral transparent core surrounded by an opaque gray fibrous coat (Fig. 1A). One of these diamonds, ON-DVK-294, has a complex coat composed of a few rings (Fig. 1B). The twelve's diamond, ON-DVK-281, is a fibrous cube. The diamonds vary in weight between 15 and 140 mg.

All diamonds were polished into 0.8-2 mm thick slabs with two parallel faces and were cleaned by HF (60%), HNO_3 (69%) and ethanol prior to analysis to remove all organic and inorganic contamination.

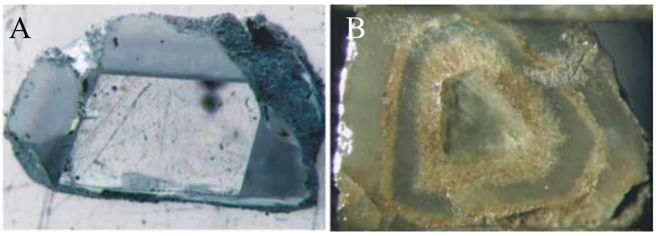

Figure 1: A. Diamond ON-DVK-276, the polished face exposes an octahedral transparent core and a gray fibrous coat. B. Diamond ON-DVK-294, the polished face exposes an octahedral transparent core and fibrous coat rings (some of them are cavity rich).

Transparent diamonds were analyzed using FTIR with a Bruker IRscope II microscope coupled to a Nicolet 740 spectrometer for nitrogen concentration and aggregation-state. The net absorption of the inclusions was obtained by subtracting type II diamond spectrum and nitrogen absorption spectra (IaA and Iab) from the original spectra. The common bands found were those of water and carbonate. The $CO_2/(CO_2+H_2O)$ ratio was calculated using estimated absorption coefficient (Navon et al., 1988).

Cathodoluminescence (CL) images of the diamond slabs were collected using Gatan MiniCL attachment. They were used as maps of the diamond internal structure.

Individual, shallow, subsurface inclusions were detected using back-scattered electron-imaging and analyzed for major element composition using a focused 15 keV, 10 nA beam of JEOL JXA 8600 electron probe micro analyzer (EPMA) with a Pioneer-Norvar EDS detector and automation system.

RESULTS

CL IMAGING

CL imaging reveals growth-lines in all diamond cores, while the coats are commonly dark. Only two fibrous zones are CL active. The fibrous cube ON-DVK-281 show concentric growth lines. In diamond ON-DVK-294 CL reviles a few brighter zones parallel to its complex ring structure. The outmost gray ring that appears uniform in Fig. 1B, is separated into two zones in CL.

FTIR SPECTROSCOPY

FTIR spectra were collected from polished sections of six diamonds that were translucent, or that included translucent zones.
The nitrogen aggregation-state in all diamonds is IaA. The nitrogen content estimated by the IR spectra is 250 to 500±10% ppm (SIMS estimation are high, 400-1300 ±10% ppm).
The two main species measured using IR spectra are carbonate and water. The carbonate main bands are at 881±0.5 cm^{-1} and 1447±3 cm^{-1} and the water main bands are 1640 cm^{-1} at 3420 cm^{-1}. The $CO_2/(CO_2+H_2O)$ ratio ranges between 0.19 and 0.47. The ratios correlate positively with the combined concentration of Ca+Mg+Fe+Ba+Na (Fig. 2).

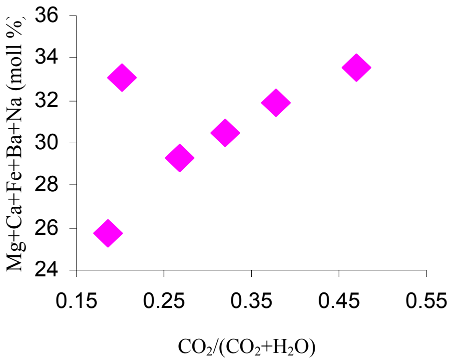

Figure 2: Molar abundance of Mg, Ca, Fe, Ba and Na (mole % as measured by EPMA) in six Canadian diamonds versus the $CO_2/(CO_2+H_2O)$ ratio (as measured by FTIR). One diamond, ON-DVK-288, is shifted from the correlation line.

Absorption lines between 900 and 1100 cm^{-1} are attributed to silicate absorption by a silicic melt, secondary phases which grew from it, or to micro-inclusions that trapped silicate minerals.

EPMA ANALYSES

EDS analysis of 512 sub-micrometer inclusions detected silicate and oxide peridotitic minerals and fluids with compositions varying between hydrous-silicic melt, carbonatitic melt and brine.

Minerals

Micro-inclusions of peridotitic minerals were identified in two diamonds. In diamond ON-DVK-276 five inclusions have Mg# of 0.92±0.01 and (Mg+Fe)/Si ratio of 1.86±0.03. These are probably olivine inclusions, the reason for the low (Mg+Fe)/Si ratio is not clear.

Diamond ON-DVK-294 carries 22 Cr-diopside inclusions. Four are mixed with brine. The Mg# is 0.95±0.04 and the Ca/(Ca+Mg+Fe) average ratio is 0.41±0.05. The Cr_2O_3 content is high, with average of 4.0±1.3 wt%. Two chromite inclusions share a Cr/(Cr+Al) ratio of 0.82. One olivine inclusion that is open to the surface has Mg# of 0.93 and (Mg+Fe)/Si ratio of 2.2. Its high fluorine content indicates contamination during sample preparation.

Fluid inclusions

Eleven on the Canadian diamonds carry micro-inclusions with compositions ranging between brine and carbonatitic melt (Fig. 3).

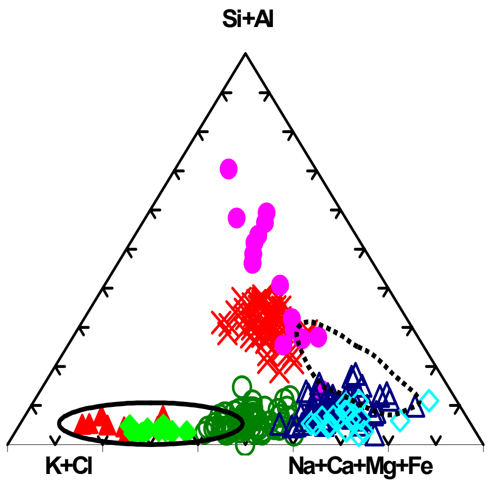

Figure 3: Brine and Melt compositions. Average Diavik brine ◆, Average Koffiefontein brine ▲, ON-DVK-294 brine ○, ON-DVK-294 carbonatitic melt △, Koffiefontein carbonatitic melt ◇, Botswanan melt ●, ON-DVK-281 melt x. Also illustrated are the Diavik brine compositional range (inside the continuous line), Koffiefontein carbonatitic to hydrous-hilicic melt (inside the dotted line).

The brine in ten of them is similar with average composition of $K_6Na_4CaMgFeBa(Si,Al)Cl_9(H_2O)_{12}(CO_3)_4$. We will refer to that composition as the "Diavik brine". K correlates positively with Cl and the average K/Cl ratio of the brine is 0.64±0.12. Na shows negative correlation with Cl and positive correlation with Mg, Ca, Fe, Ba, which also show broad negative correlation with Cl. The sodium content is approximately equal, in molar proportion, to the sum of Mg+Fe+Ca+Ba. The best negative correlation is that between Cl and the sum of all five elements. This and the positive correlation between these five elements and the $CO_2/(CO_2+H_2O)$

suggests that sodium is associated with carbonate in the Canadian brine.

In order to combine the EPMA data for the major elements with the volatile species measured using FTIR we assume that Cl^- and CO_3^{2-} compensate all positive ions. The carbonate content obtained is combined with the $CO_2/(CO_2+H_2O)$ ratio to calculate the water content of the brine (Izraeli et al. 2001).

The eleventh diamond, ON-DVK-294, carries both brine and carbonatitic melt (Fig. 4). The average brine composition is $K_{19}Na_{27}Ca_6Mg_9Fe_4Ba_3Si_4Cl_{28}$. There is a positive correlation between the K and Cl content of the micro-inclusions, and the K/Cl average ratio of this brine (0.68±0.17) is similar to that of the Diavik brine.

The Na content in ON-DVK-294 brine is much higher than that of the Diavik Brine and is almost equal to the Cl content. Mg is the most abundant element among the divalent ions. As in the Diavik Brine, Mg, Ca, Fe, Ba and Na correlates negatively with Cl and positively with their sum. No IR data is available for this opaque diamond

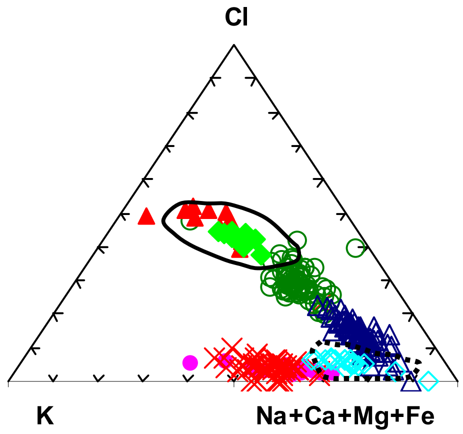

Figure 4: Brine and Melt compositions (for legend see Fig. 3).

The composition of the carbonatitic melt inclusions of ON-DVK-294 is $K_{13}Na_{24}Ca_{11}Mg_{22}Fe_5Ba_2(Si_8Al)Cl_{12}P_2$ (Fig. 4). The K/Cl ratio is 1.2±0.4 and the excess K as well as the other ions is probably balanced by carbonate. There is a positive correlation between Mg, Ca, Fe, Ba and Na and their sum.

In this diamond the brine inclusions are located in an inner growth ring and the carbonatitic melt in an outer ring (Fig. 5). In the contact area between the two zones we analyzed a few inclusions with intermediate composition. This means that brine and carbonatitic melt were not trapped in separate events. Rather, both existed simultaneously in the diamond growth environment, at least during the transition.

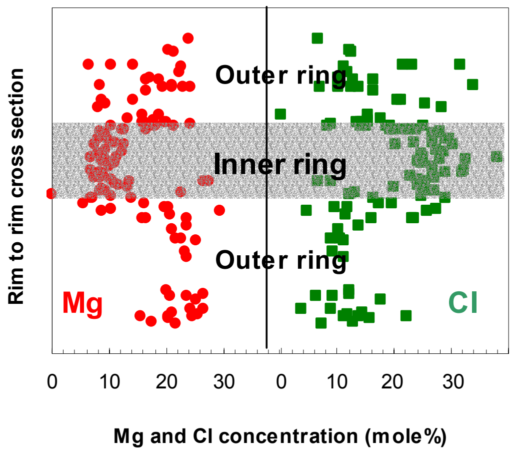

Figure 5: Mg and Cl variations along a profile on a polished face ON-DVK-294. This face does not expose the octahedral core and penetrates only two zones with different CL intensity. The brine resides in the inner zone (high Cl and low Mg concentration) and the carbonatitic melt in the outer zone (low Cl and high Mg concentration).

The twelfth diamond, ON-DVK-281 contains melt with composition that is intermediate between carbonatitic melts and hydrous-silisic melts (Fig. 3). The melt inclusions have similar composition with average of $K_{27}Na_5Ca_{14}Mg_8Fe_{10}Si_{26}Al_4Cl_3P_3$. The alkalis, divalent ions, and Si+Al account each for one third of positive ions. The diamond is opaque and no IR data is available.

DISCUSSION

Fluid micro-inclusions in diamonds trap a wide range of compositions. In most places the inclusions sample only a limited range of this variety. Zairian (Navon et al., 1988), Botswanan (Schrauder and Navon, 1994) and Brazilian diamonds (Shiryaev et al., this issue) sample compositions that lie between the hydrous-silicic and the carbonatitic end members. Eclogitic and peridotitic cloudy diamonds from Koffiefontein trapped mainly brine (Izraeli et al., 2001), but also compositions that fall along the hydrous-silicic - carbonatitic line (Izraeli et al., this issue). The Canadian diamonds display an even wider range. Most samples carry brine, but one diamond bridges the gap between brine and carbonatitic melt and another fall along the Botswanan trend.

BRINES

Brine in Canadian and South African diamonds are similar in composition. Figure 3 shows that all brines form an array extending between brine and carbonatitic melt compositions.

There is a positive correlation between K and Cl in all brines and the K/Cl ratio is similar, 0.64±0.06; 0.64±0.12 and 0.68±0.17 in the Koffifontain brine, Diavik Brine and the ON-DVK-294 brine respectively. Sodium does not follow the behavior of potassium. It correlates negatively with Cl in all suites and correlates positively with Ca+Mg+Fe+Ba. These correlations indicate that the Na is associated with the carbonatitic melt and not necessarily with the brine. The average Na/Cl ratio in the three brines varies widely, form 0.12±0.08 in the Koffiefontein brine through 0.42±0.09 in the Diavik Brine to 0.97±0.25 in the ON-DVK-294 brine.

All brines carry variable amounts of carbonate associated with Mg, Ca, Fe, Ba and Na. All these cations correlate negatively with Cl and positively with each other and with the $CO_2/(CO_2+H_2O)$ ratio. Si and Al are present, in low concentrations, in all the brines.

It worth noting that while Koffiefontein brine reside in the central clouds of octahedral diamonds, the brine in the Canadian diamonds is found in fibrous coats. This shows that coated diamonds and cloudy diamonds can grow from similar solutions.

CARBONATITIC MELTS

Information on the carbonatitic end-member comes from a few diamonds that fall near the Mg+Ca+Fe+Ba+Na apex in figure 3 and from the directions of the compositional arrays extending towards the carbonatitic melt from both brine and hydrous-silicic end members. The Canadian carbonatitic melts are unique in their strong enrichment in Na. In the Diavik brine the molar proportion of Na equals that of all the divalent ions. In the brine of ON-DVK-294 brine the Na/(Mg+Ca+Fe+Ba) ratio is ~1.2 and only in the ON-DVK-294 carbonatite the proportion of the divalent ions increases and the ratio is 0.6. All ratios are much higher than those in Koffiefontein brine and melts (all below 0.5 with average of 0.25, except one). The ratio in the carbonatitic end-member of the Botswanan melts is only 0.05.

Among the divalent ions, Mg and to a lesser extent Ca are the main ions in the ON-DVK-294 carbonatitic melt, while in the Diavik Brine all four ions appear in equal proportions. Mg and Ca are also the dominant ions in the carbonatitic end-members of Botswana and Koffiefontein, but Fe is the major divalent ion in Koffiefontein brine.

In summary, the proportions of the Na and the divalent ions vary in the different fluids and locations. Still, Mg and Ca are the dominant cations in the carbonatitic melt end-member

CARBONATITC TO HYDROUS-SILISIC MELTS

Diamond ON-DVK-281 carries melt inclusions with composition similar to that of melts from Zairian, Botwanan and Koffiefontein diamonds (Navon et al., 1988; Schrauder and Navon, 1994; Izraeli et al, this volume). The concentrations of all elements lie on the array defined by Zairian and Botswanan diamonds halfway between the carbonatitic and hydrous-silicic end-members.

No Na enrichment is apparent in the Canadian melt despite the strong Na enrichment in the Canadian brine and carbonatitic melts.

CONCLUSIONS

Diavik diamonds carry fluids representing a wide range of compositions. Most carry brine, but carbonatitic melt and intermediate composition between hydrous-silicic and carbonatitic melt are also present. Diamond ON-DVK-294 bridges the compositional gap between brine and carbonatitic melts so that all fluid inclusion data now forms a continuous array from brine to carbonatitic to hydrous-silicic composition.

Brine trapped by cloudy diamonds (Koffiefontein) and fibrous diamonds (Diavik) are similar. All fall on the above array. The detailed composition does vary between and within different localities. For example, the Canadian carbonatitic compositions are richer in sodium compares with other localities.

The coexistence of brine and a carbonatitic melt in two successive zones of the same fibrous coat and the mixed inclusions found in the narrow transition between these zones imply that the two compositions coexisted in the diamond growth zone. Most probably, the diamond grew from the brine when a carbonatitic melt penetrated and mixed with it.

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