

FLUID INCLUSIONS IN DIAMONDS - THE CARBONATITIC CONNECTION

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Fluid inclusions in diamond were first recognized by Chrenco et al. (1967) who detected carbonates and water bands in the IR spectrum of a coated diamond from Congo. Optical examination of the coat material reveals many sub-micrometer inclusions. Similar inclusions are found in many cubic diamonds and in cloudy regions within octahedral diamonds. Using TEM, Lang and Walmsley (1983) and Guthrie et al. (1991) identified apatite, quartz, mica and carbonate inside such inclusions and suggested that these are secondary phases that grew from the fluid during cooling. Navon et al. (1988), Schrauder and Navon (1994) and Izraeli et al. (2001) measured the bulk chemical composition of the micro-inclusions and showed that it varied between three end-members, one rich in Si, Al, K and water, the other in Ca, Fe, Mg, K and carbonates and the third in Cl, K and water. They suggested that these end-member compositions correspond to hydrous-silicic melt, carbonatitic melt, and brine, respectively. Here we combine these older data with other studies of coated and cloudy diamonds and with new results from Canadian, South African and Siberian diamonds and discuss possible scenarios for the evolution of these fluids, their source and their role in diamond formation.

THE COMPOSITION OF THE FLUIDS

Micro-inclusions in diamonds from Zaire, Botswana, South Africa, Brazil, India and Siberia carry melts that vary in composition between the hydrous-silicic end-member and the carbonatitic component. The hydrous-silicic end-member carry water with little or no carbonate and (on a volatile free basis) ~70 wt% SiO₂, 10% K₂O, 7-14% Al₂O₃, 0-7% FeO, a few percents of TiO₂, Na₂O and Cl and almost no MgO, CaO or P₂O₅. The carbonatitic end-member is much more variable. CaO appears in all compositions at levels of 20-25% and is accompanied by MgO (10-30%), FeO (5-20%) and K₂O (10-30%). Na₂O is present at lower levels (5-15%), TiO₂ and P₂O₅ are under 5% and Al₂O₃ is below detection limit. An exception is the Brazilian carbonatitic end-member which carries no K₂O and little MgO and is correspondingly enriched in CaO, P₂O₅ and FeO.

A third component was found in micro-inclusions from Koffiefontein and Diavik. These micro-inclusions carry brine rich in water, chlorine and alkalis and are

variably enriched in Ca, Mg, Fe, Ba and carbonate. The Koffiefontein diamonds fall close to the brine end-member that carries mostly Cl, K and Na (10:7:1 in molar proportions) and minor amounts of Fe, Ca, and Si, all dissolved in water (with H₂O/Cl molar ratio of 2-4 and almost no carbonate). The Canadian diamonds carry brine that is richer in carbonate so that a second array is defined, extending from the brine towards the carbonatitic end-member. The inclusions in one Canadian diamond extend the range close enough to the carbonatitic component. This end-member composition is broadly similar to that defined by the hydrous-silicic - carbonatitic array, but is high in BaO (9%) and Na₂O (15%).

Recently, carbonatitic and sulfide melts were found in diamonds from Yubilenaya (Klein-BenDavid et al., this volume). The sulfide melts are rich in iron and nickel with S/(S+Fe+Ni) varying continuously between 0.64 and 0.35. Carbonatitic melt was found in two micro-inclusions of a sulfide-bearing diamond and in additional diamond from that mine. Carbonate IR bands were detected in these two diamonds and in another sulfide-bearing diamond. No single inclusion exhibit mixing of carbonate and sulfide melts. The carbonatitic melt composition is similar to those from other localities.

Taken together, the carbonatitic component is associated with all other fluids, brine, hydrous-silicic and sulfide melts. Coming from all directions we obtain similar compositions with an average of ~20% MgO, 20% CaO, 10% FeO, 10% Na₂O, 20% K₂O, 10% SiO₂, 3% TiO₂, P₂O₅ and Cl, occasional BaO and no Al₂O₃ (all on carbonate and water free basis). The high alkalis/silica ratio and the low Cl content imply that K and Na in the carbonatitic melt are mostly associated with carbonate.

From the above description it is clear that the carbonatitic melt component appears together with all the other three end-members. Commonly individual inclusions trap mixtures of carbonatitic melt with either brine or hydrous-silicic melt (but not yet with sulfide melt). In other cases the two components are trapped as separate micro-inclusions in the same diamond, or in diamonds of similar morphology from the same mine. In contrast, the other components were never detected with one another in a single diamond and no mixing lines were observed between them. Even in Koffiefontein and Diavik, where we did find all three

components (in different diamonds), individual inclusions plot only along the two arrays that merge at the carbonatitic end-member composition.

Mineral micro-inclusions were also found in the fluid-bearing diamonds. In Koffiefontein Izraeli et al. (2003) found peridotitic and eclogitic minerals associated with the brine; commonly residing together in individual inclusions. The brine in peridotitic and eclogitic diamonds is of similar composition, except for sodium enrichment in the peridotitic diamonds. Only peridotitic minerals were found in Diavik, again associated with brines that are similarly enriched in sodium. Both eclogitic and peridotitic diamonds were found in Siberian diamonds (Talnikova, 1995).

CHEMICAL EVOLUTION OF THE FLUIDS

The arrays connecting the carbonatitic melt composition with the brine and the hydrous-silicic melt (Fig. 1) suggest that the three fluids are genetically related. Is it possible to derive all three from a single fluid? The best candidate for such parental fluid is the carbonatitic melt. First, this component is the only one that carries carbon that is essential for diamond growth. Second, it is always present with all other fluids, so the most straightforward evolution is from a carbonatitic melt to each of the other fluids (or to all by immiscibility).

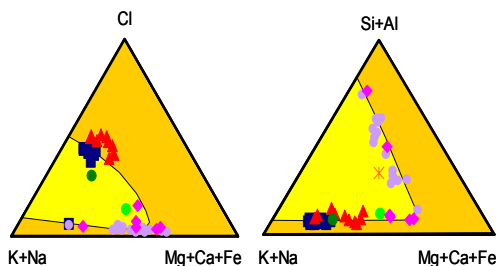


Figure 1: Average composition of micro-inclusions in world wide diamonds. Blue squares – Koffiefontein; Red triangle – Diavik brine; Green circles – ON-DVK-294; Red star – ON-DVK-281; Pink diamonds – Siberian diamonds; Purple circles – Botswanan diamonds.

How can a parental carbonatitic melt evolve to form the observed range of compositions? Previous suggestions for producing the hydrous-silicic array include (1) crystallization of carbonate from the carbonatitic melt, (2) melting of carbonated eclogite to produce first a hydrous-silicic melt that evolves towards the carbonatitic end-member with further melting, (3) mixing of two such magmas (Schrauder and Navon,

1994; Schrauder et al. 1996; Wyllie and Ryabchikov, 2000), (4) formation of both the silicic melt and the brine by immiscibility and separation of fluids formed during cooling of a parental carbonatitic melt (Perchuk et al., 2002).

CRYSTALLIZATION OF A PARENTAL CARBONATITIC MELT

Schrauder and Navon (1994) suggested that crystallization of carbonate may produce the array towards the hydrous-silicic end-member. The carbonate must remove alkalis as well as Ca, Mg and Fe; removal of additional phases is required to deplete Ti and P content. Brine production is achieved only after extensive crystallization (to bring Cl from ~3 to ~40 wt%). The fractionating carbonate must carry less alkalis and be accompanied by a silicate, phosphate and Ti-bearing phases to prevent enrichment of the corresponding oxides. The K/Cl ratio in the carbonatitic melts is ~7, and in all brine it is constant at 0.6-0.7. This requires very efficient depletion of K₂O content in the initial stages of crystallization.

MELTING OF CARBONATED PERIDOTITES AND ECLOGITES

Experimental data at pressures of 15-35 kbar (Fallon and Green, 1989; Yaxley and Green, 1994, Dalton and Presnell, 1998, Yaxley, 1999) indicate that while melting of carbonated peridotite yields carbonatitic melts, quartz eclogite would produce a limited amount of silicic melt which would evolve into a carbonatitic melt with further heating and melt extraction. While these data is consistent with derivation of the hydrous-silicic to carbonatitic melts during progressive heating and melting of carbonated hydrous eclogites, it is not easy to introduce brine production into this scenario. Brine may be present as sub-solidus fluid and evolve into a carbonatitic melt upon heating of carbonated peridotite. Brine is also associated with eclogitic minerals (Izraeli et al., 2001, 2003). Thus, in this scenario, the brine evolves in quartz-free eclogites while the hydrous silicic melt in a quartz-bearing variety. The occurrence of peridotitic minerals in micro-inclusion-bearing diamonds (Talnikova, 1995) is not explained by the melting scenario.

MIXING AND METASOMATIC INTERACTIONS

If all components are available then mixing is straightforward. The hydrous-silicic and carbonatitic components may be produced by melting, but brine production is not well understood. Metasomatic interactions between one fluid and the rocks through

which it migrates may also lead to evolution towards the other end-members.

LIQUID IMMISCIBILITY

Ternary diagrams of the major oxides of the different fluids (Fig. 1) reveal a wide compositional gap between the hydrous-silicic melts and the brine. Perchuk et al. (2002) suggest immiscibility between a silicic melt and a KCl melt. They interpret the presence of high-K clinopyroxene in diamond inclusions as evidence for the persisting of such immiscibility to high pressure. Clearly such a miscibility gap provides a perfect explanation for the observed arrays. Starting with a carbonatitic melt and crystallizing carbonates would drive the composition into the immiscible region where it would separate to yield a more silicic melt and brine. A more detailed examination demonstrates that mass balance cannot be maintained if the fractionating phase is a pure Ca-Mg-Fe carbonate, and that it must also carry alkalis (mostly sodium). This shifts the position of the fractionating assemblage in Fig. 1 to the left, from the Ca+Mg+Fe apex closer to the composition of the carbonatitic melt end-member. The bulk melt composition evolves up and to the left and separates into two immiscible fluids. Later crystallization continues from either of the immiscible fluids (e.g., the silica-rich one) would lead to further evolution towards the end-member composition with separation of more evolved brine.

Observations

In three diamonds, micro-inclusion composition varies systematically with radial position, allowing examination of the evolution of the fluid during the growth of the diamonds. Two Brazilian diamonds evolve along the carbonatitic - hydrous-silicic join (Shiryaev et al., this volume). A Canadian diamond evolves along the carbonatitic - brine array (Klein-BenDavid et al., this volume). The melt trapped in the Brazilian diamond BR-1 is more carbonatitic in the central parts and evolves into a silicic melt towards the rim. The opposite trend was detected in diamond BR-5. It is easiest to explain these opposing evolution trends by mixing. In the case of BR-1 increasing amounts of hydrous-silicic melt are introduced into a larger reservoir of carbonatitic melt; the other way around for BR-5. It is also possible to produce BR-1 by cooling and fractionation of a carbonatitic melt and BR-5 during heating. The direction of the process seems to be more robust in the case of immiscibility. The process cannot be reversed unless brine is re-introduced. However, BR-1 may be produced during

cooling and separation of immiscible fluids, BR-5 may form, when a fresh carbonatitic melt arrives and mixes with the evolved hydrous-silicic melt.

The same problem is posed by the Canadian diamond, ON-DVK-294, which carries brine in an inner zone and carbonatitic melt in the outer rim which surrounds it. The composition of the inclusions in the two zones is presented in Fig. 2. Most form two clusters (carbonatitic and brine); a few show intermediate composition. Klein-BenDavid et al. (this volume) noted that the inclusions with the intermediate composition reside near the contact between the two zones (which is clearly observed using cathodoluminescence). The presence of intermediate compositions indicates that the two clusters were not formed in separate events. The sharp transition advocates against a continuous evolution. Mixing is the best explanation for this sharp transition from brine to carbonatite. As suggested above for the Brazilian diamonds, the simplest way to introduce the two components is to let a fresh carbonatitic melt to mix with brine that evolved from a former batch.

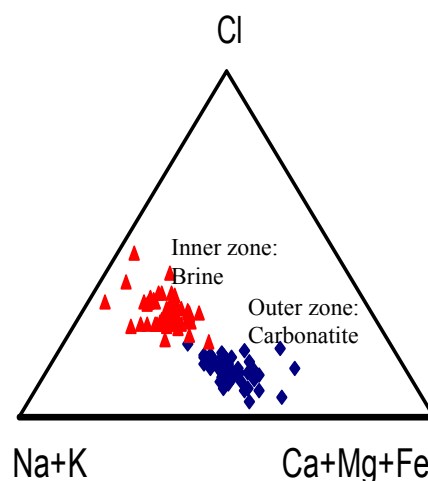


Figure 2: Diamond ON-DVK-294 micro-inclusions composition. The diamond carries brine in an inner fibrous zone and a carbonatitic melt in an outer fibrous zone.

THE ROLE OF FLUIDS IN DIAMOND FORMATION

Inclusions in diamonds provide direct information on the environment in which diamonds crystallize. Mineral inclusions indicate that most diamonds were formed in peridotitic and eclogitic rocks. Fluid

inclusions sample the medium in which their host diamonds grow. The wide range of fluids found in micro-inclusions plots along three arrays extending from carbonatitic melt towards a hydrous-silicic melt, brine and sulfide melt. The first two are continues, with inclusions spanning the full range between the end-members. No inclusions carrying intermediate compositions between carbonatitic and sulfide melt are evident in the limited data base acquired recently. The presence of carbonate in all fluids opens the possibility to grow the diamonds from the carbon they carry. Recent experimental data demonstrate that diamonds can be grown from carbonate and alkali-carbonate melts (Akaishi, 1990; Litvin, 1999; Pal'yanov, 1999). Adding water to the system enabled Pal'yanov et al. (1999) to grow diamonds at the pressures and temperatures recorded by natural diamonds. In most experiments, the source for the diamond carbon was graphite, but in others, diamonds were formed by reduction of the carbonate. These experiments clearly demonstrate the ability of the trapped fluids to grow diamonds and to catalyze growth from other carbon sources.

Fluid inclusions were found in fibrous as well as in octahedral diamonds. Some of these diamonds carry eclogitic and peridotitic minerals with compositions similar to those of the world-wide population of diamond inclusions and record similar pressures and temperatures. This indicates that the fluid-bearing diamonds grew in the same environment as most other diamonds. Inclusions of potassium-rich clinopyroxene in many diamonds call for crystallization from environment with extremely high K-activity. Perchuk et al. (2000) suggested that it reflects growth in the presence of KCl brine. Many diamond inclusions exhibit enrichments in incompatible trace elements which are commonly related to interaction with fluids. The above observations suggest that many diamonds grew from fluids, similar to those sampled by the micro-inclusions.

The low aggregation state of nitrogen in all micro-inclusion-bearing diamonds (type IaA) suggests that they are of relatively young age. This may raise doubt in the relevance of their mode of formation to older diamonds. Considering the imperfect crystalline structure of the micro-inclusion-bearing diamonds, it is possible that such diamonds grew in older times as well, but were later recrystallized or dissolved in favour of more stable crystals.

THE FLUID SOURCE

As discussed above, it is likely that the various fluids trapped in diamonds evolved from a parental carbonatitic melt. Can the source of this melt be constrained?

THE FLUIDS ARE COLLECTED FROM A LARGE RESERVOIR

The fluids are highly enriched in many trace elements. Schrauder et al. (1996) found enrichments of up to 10^3 the primitive mantle values. Turner et al. (1990) calculated enrichment of argon by a factor of 10^4 over the present mantle value. These extreme enrichments indicate that the fluids must have derived their incompatible elements from mantle volumes that are much larger than their own. Another indication of the large mantle volumes sampled by the fluid comes from the uniformity of concentration ratios of highly incompatible trace elements. Th/La, Sr/La and Ba/La ratios in fluids varying between silicic and carbonatitic melts measured by Schrauder et al. (1996) in Botswanan diamonds fall within a tight range (std < 20%, full range $\pm 40\%$). Burgess et al. (1998, 2002) and Johnson et al. (2000) noted the uniformity of Br/Cl and I/Cl ratios of many fibrous diamonds from Zaire, Botswana and Siberia. All fall within narrow ranges close to the MORB value.

Carbon and nitrogen isotopic values are also uniform. Although the general diamond population spans a very wide range of more than 30‰ in both $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$, the values recorded for fibrous, cubic and cloudy diamonds from many localities fall in a tight range: -4 to -8‰ for $\delta^{13}\text{C}$ and -2 to -9‰ for $\delta^{15}\text{N}$ (Boyd and Pillinger, 1994; Cartigny et al., 1998 and references therein). These tight ranges are consistent with derivation of the carbon and nitrogen from large enough regions so that local heterogeneities are averaged.

MORB SIGNATURE

The similarity to the MORB (or MORB source) ratios is not restricted to halogens. Carbon and nitrogen isotopic compositions are similar to that of MORB in both range and average value ($\delta^{13}\text{C} = -6\%$ and $\delta^{15}\text{N} = -5\%$). Ar isotopes also reveal MORB signature. Burges et al. (2002) noted that argon isotopic variation in fluid-bearing diamonds may be explained using three components: MORB argon, Ar produced by *in situ* U and Th decay in the diamonds and atmospheric contamination. It should be noted that the Ar and halogens are associated with the fluid while the C and N are of the host diamond. This suggests that the

ingredients for the host diamond originate at the same reservoir as the fluid. Extremely incompatible trace elements also fall close to the MORB value. The Ba/Th ratio is 82, close to the MORB ratio of 74 (but also to the continental crust ratio of 71). If less incompatible elements are included, the similarity to MORB source breaks. The Th/La, Ba/La and Sr/La ratios of the Botswanan diamonds (0.18, 14.3 and 11.5, respectively) differ from the MORB value. Ba/La and Th/La are higher than the MORB ratio Sr/La is lower. These shifts are in agreement with the higher compatibility of Ba and Th and the lower compatibility of Sr relative to La. This observed fractionation reflects the small fluid/mantle volume ratio (or very low degree of partial melt), but is compatible with derivation from a MORB source mantle.

Although the diamonds we studied originated at the sub-continental lithospheric mantle, it looks that the fluids do not reflect the heterogeneous lithosphere, but rather the larger volumes of the asthenosphere.

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