On the Connection between Fluid- and Mineral-Inclusions in Diamonds.

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As both oxidized and reduced carbon bearing species are volatile, it seems logical that fluids should play an important role in carbon transport and diamond formation in the Earth's mantle. Nevertheless, the majority of inclusion-bearing diamonds carry mineral inclusions. Fluid inclusions were found in fibrous diamonds, but the relation between these diamonds and the common, single crystal diamonds is not clear. Here we report new findings on a fibrous diamond found by S.E. Haggerty within an eclogitic xenolith and on octahedral diamonds with central, internal clouds of inclusions (cloudy diamonds). These findings help in bridging the gap between fluid and mineral inclusions in diamonds.

We analyzed the garnets and pyroxenes of a diamond-bearing eclogite from Koidu, Sierra Leone, and the inclusions found in the coat of a coated diamond enclosed in it. Electron probe analyses of the 28 microscopic inclusions yielded average solute composition of: 45% SiO_2, 2% TiO_2, 5.5% Al_2O_3, 4.5% FeO, 1% MgO, 11% CaO, 2.5% Na_2O, 23% K_2O, 5% P_2O_5, and 5% Cl. This composition is similar to that found in fluid inclusions in Zairian and Botswanan diamonds (Navon et al., 1988; Schrauder and Navon, 1994). The garnet and the clinopyroxene are similar to those found in low-Mg eclogites and in diamond inclusions. Thus, this finding connects the fluids found in fibrous diamonds with mantle eclogites and eclogitic diamonds.

Fluids (water and carbonates) are also evident in the IR spectra of eight of the ten cloudy diamonds we examined (9 from Koffiefontein, South Africa; 1 from Udachnaya, Siberia). The clouds are ~1 mm in size, occupy the central zone of the diamonds, and consist of millions of sub-micrometer inclusions.

In addition to water and carbonate, the IR spectra of the clouds reveal the presence of garnet, clinopyroxene, phlogopite, and an unidentified silicate (with a main peak at ~1010 cm^{-1}) in the different diamonds. No single diamond contains the entire assemblage. When examined with a 300μm aperture, some clouds reveal internal zoning. Electron probe analyses of individual inclusions reveal the presence of discrete mineral inclusions, wide range of fluid compositions and mixtures of the two.

Infrared spectra of KFF-202 (Fig. 1) reveal the presence of a zoned cloud with water (3450cm^{-1}), garnet (972, 906, 879 cm^{-1}), and an unidentified silicate (1007cm^{-1}). Electron probe analyses of 210 inclusions on four polished surfaces reveal wide range of compositions, varying between three end-members.

1. Eclogitic minerals - garnet with low magnesium number (mg#=0.52-0.66) and Ca/(Ca+Mg+Fe)~0.17 and clinopyroxene with mg#=0.75-0.85 and Ca/(Ca+Mg+Fe)~0.5. The Ellis and Green (1979) thermometer yields temperatures of 1008°C±50 that are ~200°C lower than eclogitic diamonds from the same mine (Rickard et al., 1986).
2. KCl-rich fluid (estimated end-member composition: 43% Cl, 34% K_2O, 8% FeO, 5% SiO_2, 4% BaO, 3% CaO, 2% Na_2O, and <1% MgO).

3. Silicate-rich fluid (45% SiO_2, 14% FeO, 14% MgO, 12% K_2O, 9% Al_2O_3, 5% Cl, and 1% CaO). This composition is broadly similar to that of the fluids found in fibrous diamonds and may be responsible for the IR peak at ~1010 cm^{-1}. Both pure end members and mixtures where found in individual inclusions.

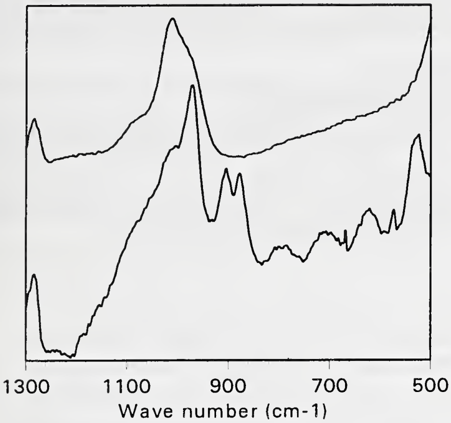

Fig. 1. Infrared spectra of two zones in the cloudy region of KFF-202 (after subtraction of diamond and nitrogen absorption). The upper spectrum shows the unidentified peak at 1007 cm^{-1}. The lower spectrum includes this peak and the three peaks of garnet at 972, 906, 879 cm^{-1}.

Infrared spectra of KFF-204 reveal water (3450cm^{-1}), garnet (972, 904, 875 cm^{-1}) and clinopyroxene (1080, 519 cm^{-1}). Electron probe analyses of 130 inclusions on 4 surfaces revealed two types of inclusions.

1. mineral inclusions with eclogitic garnets (mg#=0.67-0.84, Ca/(Ca+Mg+Fe)~0.14) and clinopyroxene (mg#=0.80-0.89, Ca/(Ca+Mg+Fe)~0.56). Thermometry yields temperatures of 1150±100°C, similar to temperatures calculated for Koffiefontein eclogitic diamonds.
2. Compositions falling along a mixing line between garnet and a Mg+Al-rich end-member (42% MgO, 37% Al_2O_3, 11% FeO, 10% CaO). At present we can offer no identification for that end-member.

Infrared absorption spectra of KFF-205, 206 and 207 show strong carbonate bands (~1440, 878 and 729 cm^{-1}) and water bands. Electron probe analyses of KFF-206 reveal a wide range of Ca-, Mg- and Fe carbonates along with SiO_2 and Al_2O_3 but little K_2O or Cl. No analysis is yet available for the other two. Garnet, clinopyroxene and high water contents were found in KFF-208; water and silicate absorption bands were found in KFF-209 (we also found a few large inclusions (10-15μm) in the transparent center of the cloud). Both IR and electron probe analyses of KFF-203 reveal only microscopic phlogopite inclusions, with mg#=0.90-0.97, at the high end of the range spanned by phlogopite inclusions in diamonds.

While all the above diamonds contain mostly nitrogen of type IaA (pairs of nitrogen atoms), one cloudy diamond (KFF-201) shows a pure IaB spectra (aggregates of nitrogen atoms). Only silicate peak at ~1010 cm^{-1} is observed in the spectrum of the cloud, with no water or carbonate. Seven inclusions were found and their electron probe analyses all yielded a uniform composition of 61% SiO_2, 33% MgO, and minor amount of FeO and CaO (Si/Mg molar ratio of 54:46).

A single cloudy diamond from Udachnaya (Schrauder et al., 1993) carries water, carbonate, and solute of 26% Cl, 31.5% K_2O, 27.5% BaO, 7.5% SrO, and minor amounts of SiO_2, FeO, CaO,

Al_2O_3 and MgO. The finding of a 10 micron olivine inclusion (Fo_{94}) within the cloudy region suggests that this diamond belongs to the peridotite suite.

The unique feature of the cloudy diamonds is the mutual occurrence of both mineral and fluid inclusions. Except from their microscopic size, the mineral inclusions are similar to other mineral inclusions in diamonds. The fluids span a wide range of compositions, much wider than that of the fluids trapped in fibrous diamonds (Fig. 2). Three types of fluids may be distinguished (although inclusions containing mixtures of these types were also observed).

1. Silica-rich composition that is broadly similar to that of fibrous diamonds.
2. Water-rich composition that is also rich in KCl (similar inclusions were also described by Chen et al., 1992).
3. Carbonate-rich fluids. Some inclusions may actually contain carbonate minerals, but the wide range of compositions and the presence of water suggest that some were trapped as fluids.

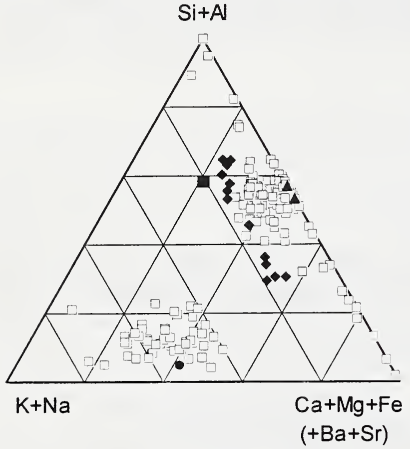

Fig. 2. Comparison of fluids in cloudy and fibrous diamonds. Open squares - individual inclusions in KFF-202, circle - cloudy diamond from Udachnaya, solid square - coated diamond from Koidu, diamonds - fibrous diamonds from Botswana (Schrauder and Navon, 1994), upper and lower triangles - clinopyroxene and garnet, respectively. Fluid inclusions in KFF-202 contain mainly the first two types of fluids; carbonate-rich fluids that fall close to the lower right apex were found in other diamonds from Koffiefontein.

The trapping of microscopic fluid- and mineral-inclusions in individual clouds (and most probably within a single micro-inclusion) indicates that diamond, garnet, and pyroxene were in equilibrium with a fluids during the growth of the diamond. The combination of diamond, carbonate, and water indicate a relatively high oxygen fugacity. However, it must be noted that not all inclusions carry carbonates. In addition, IR absorption at the 2840-2970 cm^{-1} typical of C-H bonds is present in many spectra. This may be the result of surface contamination or be due to the presence of hydrocarbons in the inclusions. We plan to conduct analyses of specially cleaned samples to check this point. The presence of water+hydrocarbon rich fluids may explain why some fluids dissolve large amounts of silica, while others carry mostly KCl.

References

Chen, F., Guo, J.G., Chen, J.C. and Liu, C.R., 1992, First discovery of high-potassium and high-chlorine in inclusions in diamond. Chinese Science Bulletin, 37, p. 1557-1560.

Ellis, D.J. and Green, D.H., 1979, An experimental study of the effect of Ca upon garnet-clinopyroxene Fe-Mg exchange equilibria. Contrib. Mineral. Petrol., 71, p. 13-22.

Navon, O., Hutcheon, I.D., Rossman, G.R., and Wasserburg, G.J., 1988, Mantle-derived fluids in diamond micro-inclusions. Nature, 335, p. 784-789.

Schrauder, M. and Navon, O., 1994, Hydrous and carbonatitic fluids in fibrous diamonds from Jwaneng, Botswana. Geochim. Cosmochim. Acta. 58, p. 761-771.