MINERAL INCLUSIONS IN CLOUDY DIAMONDS FROM KOFFIEFONTEIN SOUTH AFRICA

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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. Barometry and thermometry of such inclusions suggests that most diamonds were formed at depth of 150-250 km, in the sub-continental mantle (Meyer, 1987). Melt and fluid inclusions indicate the source from which the diamonds grow (Navon et al., 1988; Schrauder and Navon, 1994). In this work we present micro-inclusions in cloudy diamonds from Koffiefontein, South Africa. The inclusions contain minerals (Izraeli et al., 2003), brine (Izraeli et al., 2001) and carbonatitic and hydrous-silicic melt.

METHOD

Seventeen cloudy diamonds from Koffiefontein, South Africa were investigated. In each diamond two parallel surfaces were cut and polished with at least one of them intersecting the cloud (Fig. 1). The samples were cleaned using concentrated HF (60%) and HNO_3 (69%) and rinsed in water and ethanol. Infrared (IR) absorption spectra were collected using a Nicolet 740 FTIR spectrometer. Spectra were recorded with 4 cm^{-1} resolution. Net IR absorption of the inclusions was obtained by subtracting a reference Type II spectrum (a diamond with no detectable nitrogen), and the appropriate amounts of synthetic type IaA (nitrogen pairs) and IaB (nitrogen aggregates of four) spectra needed for removing the nitrogen bands. Electron probe microanalyses (EPMA) of individual sub-surface micro-inclusions were carried out using a JEOL JXA 8600 superprobe using a focused 15KeV, 10nA electron beam.

RESULTS

SAMPLES

The diamonds are 1.5-4.0 mm in size and weights between 9 and 65 mg (0.05-0.33 carat). Ten diamonds have octahedral morphology. Seven are of irregular shape, but of these, three have one octahedral face or more. They are colorless and transparent (apart from the cloudy region). The clouds are about 1 mm in size and in most cases occupy the inner part of the diamond. Fourteen diamonds contain transparent core in the center of their clouds. In a few cases the cloud extends to the diamond external faces. Each cloud consists of millions of sub-micrometer inclusions; the number density of the inclusions is not uniform within the clouds.

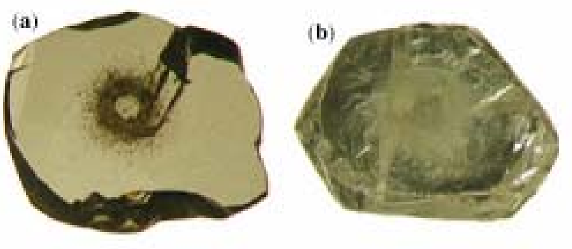

Figure 1: Binocular image of ON-KFF-166 (a) and ON-KFF-168 (b). In both cases the clouds occupy the central zone of the diamonds. They are about 1 mm in size and surround inclusion-free cores.

COMPOSITION OF THE MICRO-INCLUSIONS

FTIR spectra of the cloudy regions reveal absorption bands attributed to the presence of water, carbonate and silicates (Table 1). In some diamonds the silicates were identified as garnet and pyroxene. EPMA analyses of 1214 individual inclusions also indicated the presence of silicates, carbonates, carbonatitic melt and brine.

1. Brine inclusions were found in 13 diamonds. The brine contains 30-50wt% Cl, 22-48% K_2O, 10-25% FeO, 2-14% CaO, 2-10% SiO_2, 0-10% Na_2O, 0-6% BaO, 0-5% Ti and under 3% of Al_2O_3 and MgO. The molar (Na+K)/Cl ratio vary between 0.48 and 0.97. The amount of Cl is not sufficient for compensating all the elements that tend to form positive ions in solution and the (2Fe+2Mg+2Ca+K+Na)/Cl ratio is usually higher than 1. The detection of carbonate in the IR spectra of the clouds suggests that CO_3^{2-} ions compensate the excess of positive ions. (Izraeli et al., 2001).
2. Melt inclusions were found in three diamonds. The average melt composition is 20-25wt% CaO, 13-18% MgO, 8-12% FeO, 18% K_2O, 8-15% Na_2O, 10% SiO_2, ~4% P_2O_5, ~2% TiO_2 and Al_2O_3 and Cl under 2%. The detection of water and carbonate in the IR spectra of ON-KFF-173 and the similarity to other carbonatitic

melts in diamonds from other localities indicate that this end-member composition is a carbonatitic melt. The composition of some micro-inclusions in two of the diamonds exhibit limited mixing with a hydrous-silicic end-member, similar to that defined for the Botswanan fibrous diamonds. No minerals were observed in any of these diamonds.

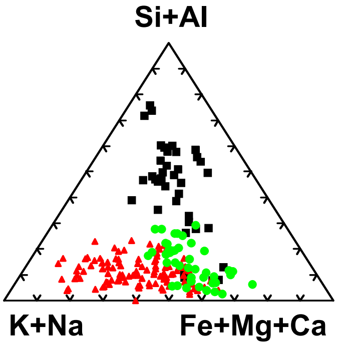

Figure 2: Fluid compositions (in molar proportion). Green circles – individual carbonatitic melt inclusion, Koffiefontein. Red triangles – individual brine inclusions, Koffiefontein (Izraeli et al., 2001). Black squares - average composition of melt inclusions in fibrous diamonds (Navon et al., 1988; Schrauder and Navon, 1994; unpublished data).

3. Carbonate minerals were identified using the combination of EPMA of single inclusions and FTIR. Some inclusions carry only Ca, Mg or Ba and carbonate bands were detected in the IR spectra of their clouds. Ca- and/or Mg- carbonates were found with both eclogitic and peridotitic minerals. Ba-carbonate was found in a single peridotitic diamond.

4. Silicate mineral inclusions observed in the cloudy diamonds belong to either the eclogitic or the peridotitic paragenesis (Izraeli et al., 2003). Mixtures of these minerals with brine (and in one case with Ba-carbonate) were observed in single inclusions. No mixing was observed between the carbonates and the brine or between the carbonatitic melt and any other phase.

4a. Peridotitic minerals

Garnet was observed in two diamonds. In one case (ON-KFF-160) it belongs to the dunitic-harzburgitic paragenesis (Mg# 78±3, Cr_2O_3 content of 6.9±1.5), in the other (ON-KFF-155) it belongs to the lherzolitic range (Mg# 84±3, Cr_2O_3 content of 4.9±1.1). A lherzolitic Cr-diopside (Mg# 93±3, Ca# 44±4, 3.3±0.6 wt% Cr_2O_3) was observed in a single diamond, ON-KFF-154. Orthopyroxene was observed in two diamonds ON-KFF-155 and ON-KFF-164 (Mg# 90±2 and 96 respectively). Olivine was observed in ON-KFF-160 ((Mg# 93±1). Peridotitic phlogopite was identified in ON-KFF-160 along with olivine and Cr-garnet.

4b. Eclogitic minerals

Garnet was observed in two diamonds. The composition of the garnet in ON-KFF-159 was restricted (Mg# 63±2 and Ca# 15±1). In ON-KFF-161 a relatively wide range was found with Mg# between 66 and 89 and Ca# between 6 and 12. Clinopyroxene was observed in 6 cloudy diamonds. Five of them spanned a narrow range of compositions (Mg# 71-91 and Ca# 38-52) and had minor Na_2O (up to 4.6wt%) and Al_2O_3 (2.7-7.9 wt%). The clinopyroxene in the 6th diamond have different composition, it has higher FeO, Al_2O_3 and Na_2O and lower CaO and MgO. High-silica mica was observed in three diamonds, two of them carrying eclogitic minerals. The silica content was higher than in most mica, 6.7±0.2 atoms per formula unit (22 oxygen basis). An unidentified Mg-Al rich phase was encountered in diamond ON-KFF-161. Twenty eight inclusions spanned a linear array between a normal eclogitic garnet and an end-member that contained no silica and consisted of ~42 wt% MgO, 39% Al_2O_3, 10% FeO and 9% CaO. The above composition and the continuous nixing line with garnet suggest identification as a hydro-garnet. However, the (Mg+Fe+Ca)/Al molar ration is 3.25/2, slightly higher than the expected 3/2 ratio in garnet and no such complete hydro-pyrope substitution is known in nature.

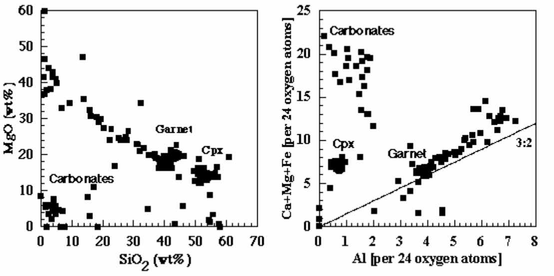

Figure 3: EPMA analyses of single inclusions in ON-KFF-161. Left - Eclogitic garnet and clinopyroxene with Ca-carbonate and an unidentified phase rich in Mg. A full mixing array connects the unidentified phase and garnet. Right – Mixing between garnet inclusions and the unidentified phase fall slightly above the (Ca+Mg+Fe)/Al=3:2 line which corresponds to hydro-garnet substitution.

DISCUSSION

Micro-inclusions in thirteen cloudy diamonds from Koffiefontein carry eclogitic and peridotitic minerals along with brine of average composition: $(K,Na)_8(Ca,Fe,Mg)_4SiO(CO_3)_4Cl_{10}(H_2O)_{28-44}$. As can be seen in Fig. 2, the brine composition varies between an end-member rich in alkalies (and Cl) and a carbonatitic end-member. In three diamonds we found carbonatitic melts that are broadly similar in composition to melts found in Botswanan and Canadian diamonds. The micro-inclusions in these three diamonds do not show any mixing with brine. The limited mixing observed is towards a hydrous-silicic end-member, known from other localities, but not encountered here.

The composition of the eclogitic and peridotitic silicate minerals found as micro-inclusions in the cloudy diamonds is similar to that of the large mineral inclusions in Koffiefontein (Rickard et al. 1989) and worldwide (Meyer, 1987).

Formation temperatures were calculated for four cloudy diamonds, two eclogitic and two peridotitic. Source pressure was calculated for a single peridotitic diamond. The eclogitic diamonds revealed formation temperatures of 1000-1200°C (Ellis and Green, 1979, at an assumed pressure of 5GPa). One peridotitic diamond revealed formation temperature of 1120±100°C (O'Neill and Wood, 1979). A second diamond yielded temperature of 1000±200°C and pressure of 4.6±0.5 GPa assuming that its Cr-diopside was in equilibrium with orthopyroxene (Nimis et al., 2000). The above temperatures and pressure are within the range found by Rickard et al. (1989) for large Koffiefontein mineral inclusions.

The clouds also carry mineral phases not detected as larger inclusions in Koffiefontein diamonds: phlogopite, carbonates, high-Si mica, and an Al-Mg-rich phase. All may be related to introduction of fluid. The presence of different micas in the two parageneses suggests that those minerals were formed not just by precipitation from the brine but rather by metasomatic interaction between the brine and the rock through which it migrated. The similarity in mineral chemistry and P-T conditions indicated by micro-inclusions in cloudy diamonds and the larger inclusions in single-crystal diamonds from Koffiefontein suggests that the cloudy diamonds were formed in the same eclogitic and peridotitic rocks that were the source of most Koffiefontein diamonds. The close association of the anhydrous silicate minerals with fluids, carbonates and Cl-bearing micas in the cloudy diamonds indicates close interaction between the peridotitic and eclogitic host rocks and the brine. The broad similarity in the composition of brine found in either peridotitic or eclogitic cloudy diamonds (Izraeli and Navon, 2001) suggests that both rocks were affected by similar brines. The possible higher Na/K ratio in brines trapped in peridotitic cloudy diamonds (Izraeli and Navon, 2001) may reflect the more incompatible behavior of Na in peridotitic host rocks. The similar P-T conditions recorded by both eclogitic and peridotitic diamonds imply that the source rocks of the two suites were not far from each other. In view of the proximity in space and in the nature of the brine, the simplest scenario is formation of both peridotitic and eclogitic cloudy diamonds in a single event. The event was significant as cloudy diamonds make up about 20% of the inclusion-bearing diamonds of Koffiefontein (Rickard et al., 1989).

Based on the above evidence we suggest that brine penetrated neighboring peridotitic and eclogitic rocks at temperatures of 1000-1200°C and pressures of 4-6 GPa. The brines carried water and dissolved salts and carbonates. They triggered diamond precipitation, mostly on preexisting, partly resorbed diamonds. The source for the carbon may have been the carbonate dissolved in the brine.

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Table 1: Mineral assemblages in Koffiefontein cloudy diamonds

name		garnet	cpx+opx +ol	mica	carbonate	Un-identified	pharagenesis	CL
KFF-156	fluid^{E,I}		cpx^{E}		car^{I}		Eclogite	Oc
KFF-157	fluid^{E,I}		cpx^{E,I}	mica^{E}			Eclogite	Oc
KFF-159	fluid^{E,I}	gar^{E,I}	cpx^{E}	mica$^{E, I}$			Eclogite	Oc
KFF-161	fluid^{E,I}	gar^{E,I}	cpx^{E,I}		Ca-Mg^{E}	AlMg^{E}	Eclogite	Oc
KFF-165	fluid^{E,I}		cpx^{E,I}		car^{I}		Eclogite	Not clear
KFF-166	fluid^{E,I}			mica$^{E, I}$			Eclogite	Oc
KFF-175	fluid^{E,I}		cpx^{E}		car^{I}		Eclogite	Cubic
KFF-154	fluid^{E,I}		Cr-cpx^{E,I}		car^{I}		peridotite	Oc
KFF-155	fluid^{E,I}	Cr-gar^{E}	opx^{E,I}		Ba^{E}+car^{I}		peridotite	No zoning
KFF-160	fluid^{E,I}	Cr-gar^{E}	oliv^{E}	phlog$^{E, I}$			peridotite	No zoning
KFF-164			opx^{E,I}		Ca-Mg^{E}+car^{I}	SiCaMg^{E}	peridotite	Oc
KFF-162	fluid^{E,I}				car^{I}		un-known	Cubic-Oc
KFF-163	fluid^{I}				Ca-Mg^{E}		un-known	Oc
KFF-176	fluid^{E,I}					SiAlFe^{E}	un-known	Not clear
KFF-168	melt^{E}				car-melt^{E}		un-known	Oc
KFF-172	melt^{E}				car-melt^{E}		un-known	Not clear
KFF-173	melt^{E,I}				car-melt^{E}+car^{I}		un-known	Not clear

Cr-gar - chrome garnet, opx - orthopyroxene, Cr-cpx - chrome clinopyroxene, oliv - olivine, phlog - phlogopite, gar - garnet, cpx - clinopyroxene, Ba - barium, Ca-Mg - analyses of only calcium and/or magnesium, car - carbonate, silic - silicate with IR peak at 1010 cm^{-1} , car-melt – carbonatitic melt, AlMg - unidentified phase consists of ~42% MgO, 39% Al_2O_3, 10% FeO and 9% CaO, CaSiMg - unidentified phase consists of 51 wt% SiO_2, 40% CaO and 8% MgO. SiAlFe - unidentified phase consists of ~ SiO_2 33 Wt%, Al_2O_3 20%, FeO 27%, MgO 12% and CaO 4%.

CL – cathodoluminescence, Oc – octahedral, E - observed by electron probe micro-analysis, I - observed by infra-red spectroscopy.

pyroxene was identified by Infra-red spectroscopy, the classification between clino- and ortho-pyroxene was done using the electron probe micro-analysis. Mica – A peak at 1010 cm^{-1} was detected by IR in diamonds carrying either high-silica mica or phlogopite.

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