Comparison between LA-ICP-MS and EPMA analysis of trace elements in diamonds

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ABSTRACT

Eight elements were measured in twenty-eight microinclusion-bearing diamonds using both Electron Probe Micro-Analyzer (EPMA) and the cellulose-calibrated Laser Ablation Inductively Coupled Plasma Mass Spectrometry (LA-ICP-MS) methods. Orthopyroxene microinclusions (<1 μm) found in one of the diamonds have very similar Si atoms per formula unit and Mg/(Mg+Fe) ratios to those of larger orthopyroxene inclusions in diamonds, indicating that the EPMA analysis of the major elements in individual mineral and fluid microinclusions is accurate to better than 15%. For the fluid-bearing diamonds, very good correlations were found between the element/Fe ratios determined by EPMA and LA-ICP-MS for Mg, Ca, Na and K and most diamonds fall on or close to the 1:1 line, validating the accuracy of both techniques. Al/Fe, Ti/Fe and Ba/Fe ratios show good to moderate correlations. LA-ICP-MS analyses of four coated diamonds show that concentrations in the microinclusion-bearing coat are higher than those in the clear core by two orders of magnitude or more. Since most interferences from C–N–O–H molecular ions can be corrected by reference to analyses of pure synthetic diamond, and fewer interferences are expected for the heavier trace elements, the assembled information suggests that LA-ICP-MS technique combined with the cellulose calibration method provides accurate trace-element analyses of diamonds and allows compositional characterization of fluids trapped in them.

1. Introduction

The determination of the trace-element contents of diamonds is a longstanding goal that has challenged many analysts since the first modern determination by Williams (1932, as quoted in Bibby, 1982). The trace-element contents can provide important clues to the origin of natural diamonds, including their host rocks, the nature of the medium from which they grew and the processes of growth. Trace-element data also have commercial applications in exploration and in the diamond trade. In principle, they can be used to trace the source of alluvial diamonds, to identify the country of origin of "conflict" diamonds, to distinguish between synthetic and natural diamonds and even to fingerprint individual valuable stones.

Impurities can occur in diamond in two principal ways. Foreign atoms can substitute for carbon atoms in the diamond lattice, or enter as single interstitial atoms. Alternatively, foreign material may be trapped as distinct phases and form inclusions of varying size and composition. The most common atomic substitution is nitrogen, but boron, oxygen and nickel are also reported (Sellschop, 1979; Bibby, 1982; Zaitsev, 2001). Hydrogen also enters atomic-level centres as substitution or interstitial atoms.

The most common trapped phases in diamonds are mineral inclusions that are similar to the common peridotitic or eclogitic assemblages of mantle rocks. Their size varies from a few hundred micrometers down to a few hundred nanometers and possibly even smaller. Fluid inclusions have also been found in diamonds (e.g., Tomilenko et al., 1997). Most common are the sub-micrometer inclusions that populate the fibrous matrix of cubic diamond and the coats of coated diamonds. Fluids have also been found in microinclusions that form clouds inside otherwise clear diamonds.

Fesq et al. (1975) used neutron activation analysis (NAA) to determine the bulk trace-element contents of diamonds. They noted that brown and green diamonds have higher impurity levels than yellow or colourless diamonds. Even higher concentrations were reported by Bibby (1979) who found sub-ppm levels of REE in the coat of a coated diamond. Both suggested that the impurities reside in sub-microscopic inclusions. Lang and Walmsley (1983) described sub-rounded inclusions up to 1 μm in diameter in a coated diamond. Using infrared (IR) spectroscopy, Chrenko et al. (1967) noted the presence of IR absorption bands of water and carbonates in a coated diamond. Navon et al. (1988) used IR and secondary-ion mass spectrometry (SIMS) to determine the major-element composition of such micro-inclusions and suggested that the trapped material represents the fluids from which the diamonds grew. Later, Navon and coworkers used the Electron Probe Micro-Analyzer (EPMA) to determine the bulk composition of many individual microinclusions in each diamond and combined the average composition of the major oxides with the IR

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Table 1
Diamond characteristics

Sample	Origin	Morphology	Colour	Weight (mg)	Dimensions (mm)	Habit	Fluid type [a]
ON-DBP-330	DeBeers Pool [b]	Broken cube	Gray-white	92.7	2.4–3.2	Fibrous/polycrystalline	Sal–Carb
ON-DBP-331	DeBeers Pool	Broken cube	Gray-white	119.7	2.8–3.8	Fibrous/polycrystalline	Sal–Carb
ON-DBP-332	DeBeers Pool	Anhedral	Gray-white	69.4	2.1–4.6	Fibrous	Sil
ON-DBP-335	DeBeers Pool	Broken cube	Gray-white	20.9	1.2–3.4	Fibrous/polycrystalline	Sal–Carb
ON-DBP-337	DeBeers Pool	Broken cube	Green-gray-white	61.1	2.3–4.3	Fibrous/polycrystalline	Sal–Carb
ON-DBP-338	DeBeers Pool	Anhedral	Green-gray	30.9	2–2.8	Coated cube	Sal–Carb
ON-DBP-339	DeBeers Pool	Broken cube	Gray-white	14.6	3.1–3.5	Fibrous/polycrystalline	Sal–Carb
ON-KNG-367	Koiingnaas [b]	Anhedral	Gray-white	113.4	3.4–4.6	–	Sil
ON-KAN-381	Kankan [b]	Oval	Green-white	41.5	3–3.1	Coated	Sil–Carb
ON-KAN-382	Kankan	Oval	Green-white	26.8	2.5–2.5	Coated	Sil
ON-KAN-383	Kankan	Oval-Octahedral	Yellowish-green	24.1	2.1–2.3	Coated	Sil–Carb
ON-KAN-384	Kankan	Octahedral?	Milky-white	25.9	2.1–2.3	Coated	Carb
ON-KAN-386	Kankan	Octahedral	Milky-white	41.2	2.4–2.8	Coated	Carb
ON-KAN-388	Kankan	Anhedral	Milky-white	27.1	2.1–3.2	Coated	Carb
ON-KAN-389	Kankan	Anhedral	Milky-white	16.5	1.5–1.6	Fibrous — cloudy	Carb

[a] Fluid type: Carb = carbonatitic, Si = silicic and Sal = saline.
[b] Approximate source localities: DeBeers Pool: 28°40′S, 24°40′E; Koiingnaas: 30°10′S, 17°20′E; Kankan: 10°20′N, 9°20′W.

data on the volatiles to determine that the microinclusions represent trapped high-density fluids (HDF). In some cases, microinclusions that carry minerals or mixtures of HDF and minerals were also found. The composition of the trapped HDFs varies between three end-members: a carbonatitic end-member rich in Ca, Mg, Fe, K and carbonate (CO_3^{2-}); a hydrous-silicic end-member rich in Si, Al, K and water; and a hydrous-saline fluid rich in Cl, K, Na and water (Navon et al., 1988; Schrauder and Navon, 1994; Izraeli et al., 2001; Shiryaev et al., 2005). Klein-BenDavid et al. (2007) suggested that the three end-members are genetically connected and that the silicic and the saline HDFs evolved from carbonatitic ones by crystallization and liquid immiscibility.

The trapped material amounts to less than 1% of the diamond by weight, even in zones that are highly populated by microinclusions. Thus, the common major elements, such as Si or Mg are present at trace levels in the diamonds. Nevertheless, we will retain the use of "major elements" for the main constituents of the inclusions and "trace elements" for all the rest.

Accurate analysis of trace elements such as the REE and HFSE is necessary for further development of diamond growth models. Akagi and Masuda (1988) burned cubic diamonds from Zaire and measured their Sr isotopic composition and REE, Sr, Rb, K and Ba concentrations using isotope dilution analysis. Schrauder et al. (1996) used Instrumental Neutron Activation Analysis (INAA) to measure the concentrations of 31 elements in coated diamonds from Jwaneng, Botswana. Both techniques are destructive, require a significant amount of material for a single analysis and involve a long preparation process. Furthermore, only the average composition of the bulk diamond can be determined by these techniques with no possibility to trace fluid evolution during diamond growth.

Laser Ablation Inductively Coupled Plasma Mass Spectrometry (LA-ICP-MS) is a rapid and very sensitive analytical technique for the in-situ microanalysis of solids. In principle it is a destructive method, but it leaves an ablation pit that is only ~100 μm across and 50–100 μm deep. Wang et al. (2003) used LA-ICP-MS for a qualitative analysis of the major and trace elements present in a large coated diamond from the Congo. Tomlinson et al. (2005) gave a semi-quantitative estimate of the composition of microinclusions in five coated diamonds from Congo, using the NIST Standard Reference Material (SRM) 612 as an external standard for LA-ICP-MS analyses. They used no internal standard and thus could not quantify the absolute impurity concentration in the diamond. Rege et al. (2005) used trace-element-doped cellulose (poly-$C_6H_{12}O_5$) as an external standard and the diamond carbon itself as an internal standard for the LA-ICP-MS analyses of >30 elements in two Jwaneng diamonds that were previously analyzed by EPMA and INAA (Schrauder and Navon, 1994, Schrauder et al., 1996). They found very good correlation between the

three methods for most elements and concluded that their calibration technique can be used for accurate and precise quantitative determination of trace-element concentrations in diamonds.

Trace-element geochemistry is a key to understanding magmatic processes and the evolution of diamond-forming fluids deep in the Earth's mantle and quantitative trace-element analysis is required for the modelling of such processes. Here we report EPMA and LA-ICP-MS analyses from 28 microinclusion-bearing diamonds. The EPMA analyses provide the composition of individual microinclusions, whereas the LA-ICP-MS data represent the average of about 10^6 such inclusions.
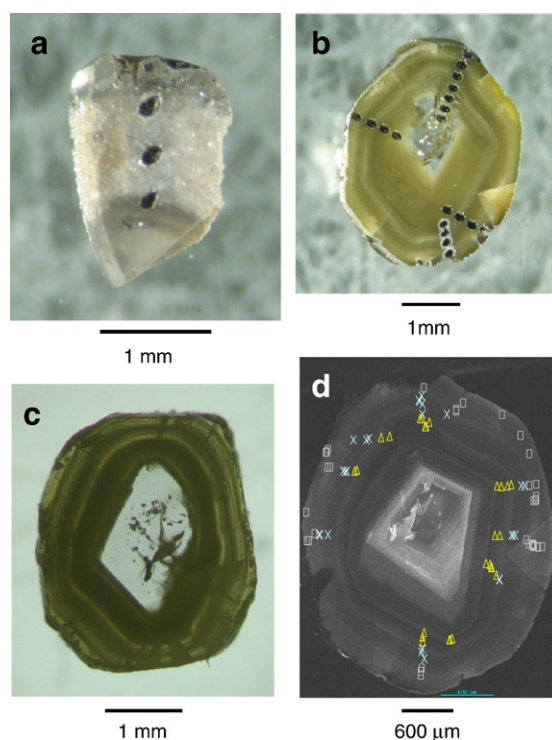

Fig. 1. Three microinclusion-bearing diamonds from DeBeers Pool and Kankan. (a) Diamond ON-DBP-335 showing the inner part and the sugary outer part that characterizes most of the analyzed DBP diamonds. The three holes were excavated during laser ablation analysis. (b) Diamond ON-KAN-381 after laser ablation analysis showing the octahedral clear core surrounded by the zoned microinclusion-bearing coat. (c) Diamond ON-KAN-383 showing a core with large mineral inclusions and zoned coat with microinclusions. (d) Cathodoluminescence (CL) image of diamond ON-KAN-381 showing the zoned coat and the location of the microinclusions analyzed by EPMA. The various symbols mark the location of the inclusions in the three concentric zones.