Trace element analyses of fluid-bearing fibrous diamonds from Jwaneng (Botswana) by neutron activation analysis

M. Schrauder
C. Koeberl
Institute of Geochemistry, University of Vienna, Vienna, Austria

Introduction

Diamonds provide valuable information about the fluid regime of the mantle. Trace element concentrations, which are attributed to impurities in diamonds, have been the subject of earlier studies by neutron activation analysis (Fesq *et al.*, 1973; Bibby, 1979). Following these investigations, Navon *et al.* (1988) were able to recognize that most of the impurities, which were attributed earlier to the diamond itself, are actually located in micro- inclusions. These micro-inclusions contain mantle fluids that vary in their composition linearly betweena carbonatitic and a hydrous endmember (Schrauder and Navon, 1994).

Neutron activation analysis (NAA) is a powerful tool for the determination of the bulk trace elemental content of a diamond, because the carbon matrix itself is 'transparent' to neutrons. Thus, clean sample preparation is necessary. Recent improvements in detector technology make it possible to lower detection limits and to determine trace element abundances even in 'clean' diamonds devoid of visible inclusions (Hart *et al.*, 1991).

Bulk analyses of diamonds have previously been carried out with a variety of techniques, but a precise description of the analyzed material was often lacking . In this study, we analyzed thirteen diamonds of cubic shape and fibrous internal texture from Jwaneng, and one clear octahedron as a blank sample. The diamonds were characterized optically and by infrared (IR) spectroscopy and studied by electron microprobe (EMP) and proton microprobe before NAA (Schrauder and Navon, 1994; Navon *et al.*, in prep.).

Experimental technique

Fourteen diamond samples were broken in an Aluminum mortar, clean pieces with no visible cracks were selected (10–60 mg), and boiled in teflon beakers in HF, $HF + HNO_3 + HCl$, and water. Subsequently, they were irradiated in the Astra-type reactor at the Forschungszentrum in Seibersdorf (Austria) for about 5.5 hours at a flux of about 6.1013 n $cm^{-2}s^{-1}$. The samples were acid-cleaned again with acids after the irradiation. The samples were counted for 3–6 hours in the first counting period, 6-12 hours in the second counting period, and 24–72 hours in the third counting period using a high purity germanium detector (HpGe; EG&G Ortec) with 48% relative efficiency and 1.82 keV energy resolution at 1332 keV. For more details on instrumental neutron activation and techniques, see Koeberl (1993). As standards and flux monitors geological standards [two granites (G-2; ACE), and a meteorite (Allende) were used.

Results

The concentrations of the following elements were determined: Na, K, Sc, Cr, Fe, Co, Ni, Zn, As, Br, Rb, Sr, Zr, Sb, Cs, Ba, La, Ce, Nd, Sm, Eu, Gd, Tb, Yb, Lu, Hf, Ta, Ir, Au, Th and U. The total concentrations in different samples vary between 20 to 800 ppm. As the concentration of fluids in the diamonds is not known, but the concentrations of Na, K, and Fe had previously been determined in the fluid inclusions by EMP, the K abundances were used to correlate the two data sets. The potassium values obtained by NAA were normalized to the EMP values. The same normalization factors were used for the other elements. A comparison of the Na and Fe concentrations calculated from the NAA data showed excellent agreement with the EMP results.

The elements can be grouped into those that most probably reside in the micro-inclusions (i.e., in the fluid) and those that seem to be associated with the diamond matrix itself, mineral inclusions, or contamination (e.g., Au, Ir).

All samples show high enrichments of K and other incompatible elements (e.g., Ba, 0.6–0.4 wt%; Br about 50–20 ppm, Cs, 30 ppm; Rb, 1000-500 ppm; Sr, 0.5–0.2 wt%; Sc, 50–20 ppm; Zr, 2000 ppm; Hf and the light *REEs*) in the trapped fluids. All elemental concentrations show a negative correlation with the SiO_2 contents of the fluids. This trend indicates that the diamonds that host the carbonate-rich fluids are the ones that are most enriched in incompatible elements.

Strontium and Ba concentrations are generally high, show a negative correlation with the silica content, and the abundances of both elements are higher by factor of 2-5 than in kimberlites. The Sr/Ba ratio is close to 1, which is similar to kimberlites, lamproites and crust. Rubidium values are about 1000 ppm in the carbonate rich endmember and decrease towards the hydrous endmember to about 500 ppm. The Rb/Sr ratios are around 0.2. Zinc contents (about 500 ppm) are also negatively correlated with the silica content. Zircon, Th, and U concentrations are high: > 1000 ppm, > 30 ppm, and > 10ppm, respectively. Tantalum concentrations are between 4 and 12 ppm, and Sb concentrations at about 4 ppm. The contents of the siderophile elements, such as Ni and Co are relatively high at 1000 and 100 ppm, respectively. The concentrations of both elements do not correlate with the silica content. Chromium concentrations are about 500 ppm. Lanthanum concentrations decrease from 600 ppm in the carbonatitic endmember to 300 ppm in the hydrous endmember. The trapped fluids show steep sub-parallel chondrite-normalized *REE* patterns, with La/Yb ratios between 30 and 80. The La/Yb ratios of the fluids are lower than those observed in carbonatites, but are comparable to those of kimberlites and alkali-basalts.

Discussion

Previous electronprobe and infrared data have shown a wide range of compositions between a hydrous and a carbonatitic endmember (Schrauder and Navon, 1994). The overall high concentrations of incompatible trace elements in diamonds containing hydrous and carbonatitic fluids imply that such fluids represent excellent metasomatizing agents. The concentrations of incompatible trace elements in the fluids are higher than those of most mantle-derived rocks and vary linearly between the two endmembers. However, a similarity of the compositional signature of the fluid with deep-seated magmas (e.g., kimberlites) is observed. The ratio of La to Th, both incompatible elements, varies between 5 to 6. This ratio is closer to that of lamproites than to primitive mantle, kimberlites, or basalts. The K/Rb ratio in the fluids is around 250, which is similar to that of kimberlites, lamproites, and crustal rocks, but rather different from that of primitive mantle and basalts. The Rb/Th ratios vary over a range between 5 and 15. The U/Th ratios (1.6–4) and Th/Cs ratios (3–7) are both closer to those of kimberlites than those of lamproites. The Sr/Ba ratios (~1) are similar to those of kimberlites, lamproites, and crustal rocks. The high La/Sc ratios (6–16) are typical for deep-seated melts. The La/Yb ratio in the fluid is lower than that in carbonatites, kimberlites, and lamproites, but the *REE* patterns are steeper than in other magmas. Clearly, the geochemistry of these fluids has an affinity to deep- seated magmas, such as kimberlites, lamproites, and carbonatites.

Experimental trace element partition data (Brenan and Watson, 1991) indicate that at pressures of 1–1.5 GPa many trace elements do not partition into hydrous fluids to the same degree as into carbonatitic and silicate melts. If extrapolated to higher pressures, this trend might be the reason for the negative correlation of most of the trace elements with silica.

The fact that most of the elements determined in this study show an incompatible behaviour, are extremely enriched in the fluid, together with the low contents of compatible elements, make it difficult to constrain the parent-rock environments from which the fluids formed. Although siderophile elements, such as Ni, Co, and Cr, may behave in a more compatible way, they do not allow us to place any constraints on the source lithology. The major and trace element composition of the fluids confirms that at high pressures of the diamond stability field, both carbonatitic and hydrous fluids can be effective carriers of incompatible elements and play an important role in mantle metasomatism.

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