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Trace-element Geochemistry of Diamond

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Quantitative trace-element analyses of > 40 elements in >500 diamond (diamondite, fibrous and monocrystalline); have been carried out by LAM-ICPMS, using a multi-element-doped cellulose standard; detection limits range to low-ppb levels for many elements (Rege et al., 2005). These trace elements are present in microscopic and submicroscopic inclusions that are believed to represent the fluid from which the diamonds have crystallised.

Diamondites

In general the trace-element patterns of the peridotitic and eclogitic diamondites show enrichment of the LREE compared to the MREE with abundances continuously decreasing from Ba to Ho. Pb and Cu are enriched relative to Fe. Ti, Zr and Hf are depleted, and Nb, Ta, Th and U are enriched, relative to chondrites.

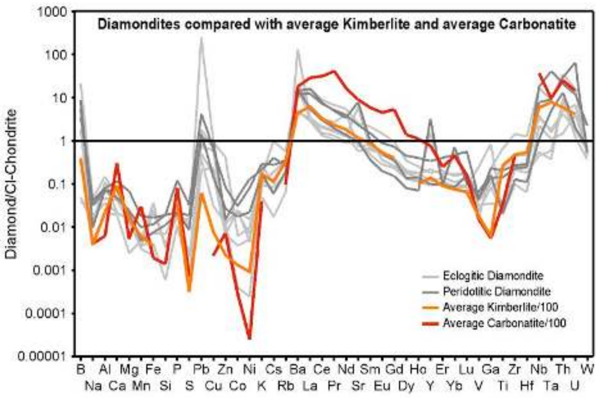

Fig. 1 Comparison of Chondrite-normalised trace-element patterns for Average Peridotitic and Average Eclogitic diamondites with Average Kimberlite and Average Carbonatite. (Data for B, Si, S and P are semi-quantitative only)

The results (Rege et al., 2008) show that peridotitic and eclogitic diamondites (polycrystalline diamonds or framesite) have probably formed from the same type of fluid(s), with trace-element and major-element distribution comparable with a kimberlitic-carbonatitic fluid. Spikes in the time-resolved signals suggest the presence of several, probably submicroscopic, solid phases (garnet, clinopyroxene, Y-Yb rich fluoride phase, Cu-Pb-Zn-Co-Ni sulphide phase, LIMA-type phase, a carbonate phase, ilmenite, chromite, mica), inferred to have crystallised from the fluid that deposited the diamond matrix. Small differences in Sr, Y and Yb, anomalies, Nb/Ta ratios and abundances of Cr, Mn, Co and Ni between the P and E type diamondites suggest that the fluid may have evolved from "peridotitic" to "eclogitic" by the removal of chromite ± sulphide ± ilmenite.

Fibrous diamonds

Some fibrous diamonds have distinctive TE patterns, with the cores displaying LREE-enriched patterns (broadly similar to the TE pattern observed for the diamondites), whereas the rims have patterns that resemble those of monocrystalline diamonds (see below), suggesting that individual stones grew from an evolving fluid. Significant differences are also seen from locality to locality, suggesting that the fluids from which the fibrous diamonds grew vary in composition from place to place.

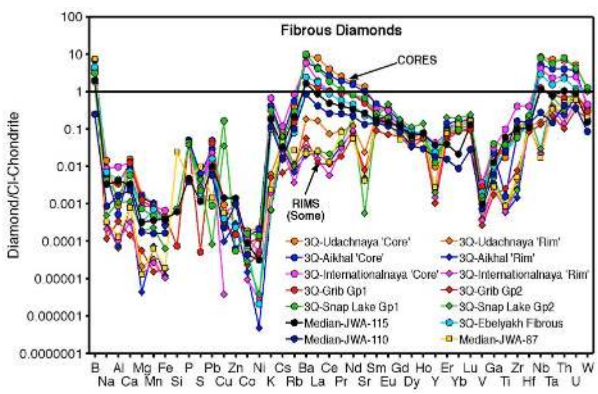

Fig. 2 Chondrite-normalised trace-element patterns of fibrous diamonds. (Data for B, Si, S and P are semi-quantitative only)

Monocrystalline diamonds

Monocrystalline diamonds in general show relatively flat to LREE-depleted REE patterns, with negative Ce, Y and Sr anomalies, Co/Ni >1 and fractionated HFSE. Strong similarities between the TE patterns of peridotitic and eclogitic diamonds from single localities suggest that the fluids from which diamonds of these two parageneses grew are essentially identical. This would imply that interaction between the fluid and the diamond host rocks is minimal, and suggests high fluid/rock ratios.

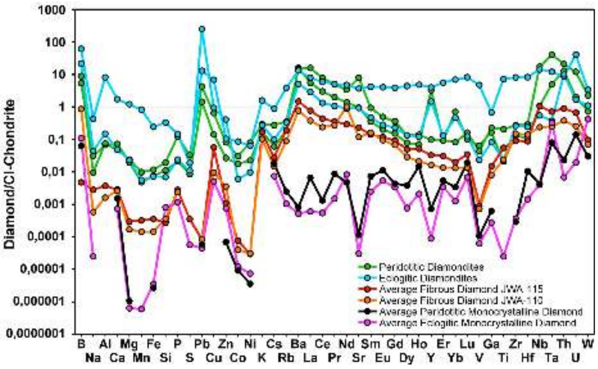

Fig. 3 Average Peridotitic and Eclogitic Diamondites, Average Fibrous Diamonds JWA-110 and JWA-115 and Average Peridotitic and Eclogitic Monocrystalline diamonds from Botswana. (Data for B, Si, S and P are semi-quantitative only)

Based on their trace-element patterns, the monocrystalline diamond samples could be roughly separated into two groups: **GrUIPLSJ** (Grib, Udachnaya, Internationalnaya, Komsomolskaya, Aikhal, Lac de Gras, Snap lake, Premier and Jagersfontein and possibly Finsch, Koffiefontein, Bingara, Argyle and Wellington) and **DOJKZC** (Dalnaya, Zarnitsa, Jwaneng, Orapa, Kelsey Lake, Liaoning, Hongqi and Shengli); the principal differences being that most of the samples in the first group show depletion in the LREE relative to the HREE and MREE and have higher overall REE abundances than the second group, which have flatter trace-element patterns and show slight negative anomalies in Yb. In each group, diamonds of peridotitic and eclogitic parageneses have the same patterns.

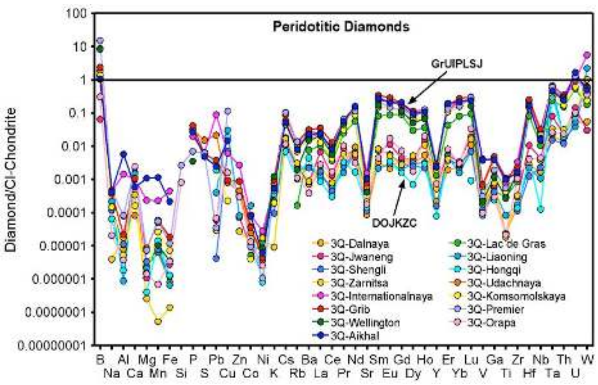

Fig. 4 Chondrite-normalised trace-element patterns of Peridotitic Monocrystalline diamonds showing the two groups – GrUIPSJ and DOJKZC. (Data for B, Si, S and P are semi-quantitative only)

Discussion

The formation of polycrystalline, fibrous and monocrystalline diamonds can be explained by the evolution of a single generalised parental fluid that had a trace-element pattern similar to kimberlite or carbonatite, but which shows significant compositional variation from locality to locality. This fluid/melt is inferred to have formed by the interaction of a CH_4-H_2 fluid with peridotite in the lithospheric mantle.

Diamondites and the cores of many fibrous diamonds may have crystallised directly from this kimberlitic-carbonatitic fluid. The ubiquitous development of pronounced negative Y anomalies (relative to Ho-Dy) may reflect the separation of fluoride phases or immiscible fluoride melts; microinclusions with positive Y anomalies are observed during ablation of diamondites.

However, many fibrous/particulate diamonds show an abrupt change in trace-element patterns as crystallisation proceeds. Strong fractionations in the REE and HFSE are difficult to explain by fractional crystallisation, but can be modelled as the result of liquid immiscibility: a separation into broadly hydrous-silicate and carbonatite fluids. This is consistent with observations of carbonate-silicate immiscibility in melt inclusions trapped in Cr-diopside derived from ca 180 km beneath the Slave craton (van Achterbergh et al., 2002).

Despite significant variation from one deposit to another, nearly all monocrystalline diamonds show low LREE/HREE, Ba/MREE and Sr/MREE, as well as low (subchondritic) Nb/Ta and Zr/Hf, suggesting that they have crystallised from the hydrous-silicate member of the proposed immiscible-liquid couple. Crystallisation of mica minerals in some sample suites (fractionation of Rb from Sm) and the fractionation between Cs and Rb, and between LREE and Ba, suggests a further separation into a hydrosilicate fluid and a brine.

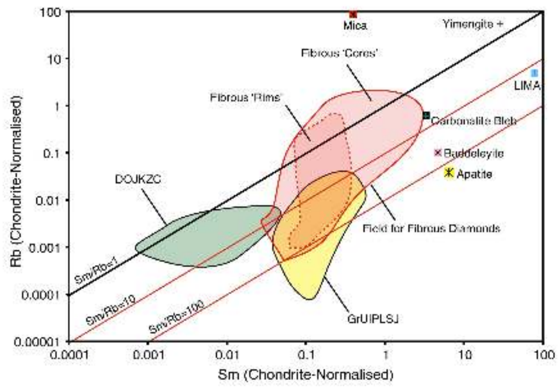

Fig. 5 Plot of Sm vs. Rb (chondrite-normalised) for Fibrous and Monocrystalline Diamonds.

Modelling of the conjugate Mg-rich "carbonatite" fluid shows it would have extremely high LREE/HREE and Sr. The reaction of this fractionated carbonatitic fluid with chromite + olivine + opx can produce subcalcic Cr-pyrope garnets (G-10 garnets) with "sinuous" REE patterns and high Sr contents, which are a characteristic inclusion in diamonds of the peridotitic paragenesis, providing a genetic link between diamonds and their most common indicator minerals (Malkovets et al., 2007).

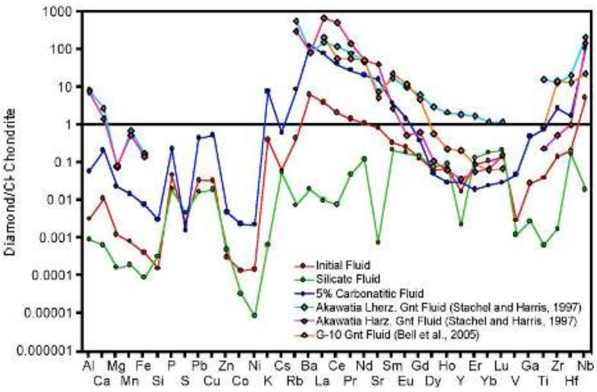

Fig. 6 Compositions of melts in equilibrium with harzburgitic and lherzolitic garnet inclusions in diamond compared with the ‘initial’, ‘silicate’ and ‘carbonatitic’ fluids. (Data for Si, S and P are semi-quantitative only)

We therefore suggest that the development of immiscibility during the evolution of low-volume melts of the kimberlite-carbonatite spectrum produces conjugate fluids, one of which crystallises most monocrystalline diamonds, and the other of which interacts with mantle harzburgites to produce the most ubiquitous inclusions in peridotitic diamonds. Preliminary comparative studies show little difference in the trace-element patterns of peridotitic and eclogitic diamonds from single localities. This implies limited interaction between fluid and wall rock, which in turn suggests high fluid/rock ratios during diamond crystallisation.

Refererences

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