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"TABLES" VS. "BENCHES" : TRACE ELEMENTS IN FIBROUS DIAMONDS

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INTRODUCTION

Fibrous and cloudy diamonds encapsulate pristine high-density fluids (HDFs) of high-Mg carbonatitic, low-Mg carbonatitic to silicic and saline compositions (Navon et al., 1988; Weiss et al., 2009 and references therein).

Following the early neutron-activation work of Fesq et al. (1975) and Bibby (1979), Akagi and Masuda (1988) and Schrauder et al. (1996) measured the concentrations of many traceelements in fibrous diamonds from Jwaneng, Botswana and Zaire, respectively. Both studies demonstrated that the HDFs have elevated levels of incompatible elements compared to primitive mantle (PM) values and that the REE patterns are similar to those of kimberlites. In the last few years, with the development of laser ablation, many more data were collected using "on-line" and "off-line" ablation methods (Resano et al., 2003; Rege et al., 2005, 2010; Tomlinson et al., 2005, 2009; Zedgenizov et al., 2007, 2009; Klein-BenDavid et al., 2010; McNeill1 et al., 2009; Weiss et al., 2009; Araújo et al., 2009). In general, all studies have found similar trace-element patterns with fractionated REEs and variable negative anomalies (PM normalized) of the alkalis (K, Rb and Cs), high field strength elements (HFSE: Zr, Ti, Nb, Ta), Sr and Y compared to elements of similar compatibility. However, only a few of these studies presented the full majorelement composition along with the trace-element data.

Weiss et al. (2011; 10IKC abstract No. 187) characterized the differences in trace-element patterns between high-Mg carbonatitic HDFs from Udachnaya, Siberia and Kankan, Guinea and pointed out their close similarity to Group I and Group II kimberlites, respectively. In the present study we closely examine the trace element compositions of microinclusion-bearing diamonds that trapped low-Mg carbonatitic to silicic and saline HDFs and use the data to explore the potential sources of diamond-forming fluids and to better understand the processes that created their specific chemical trace-element patterns.

SAMPLES

Fifteen fibrous diamonds were selected for this study: 5 from Diavik, Canada (DVK); 3 from Kankan, Guinea (KAN); 2 from Jwaneng, Botswana (JWN); 3 from DeBeers-Pool (DBP) and 2 from Koingnaas (KNG), both in South Africa. The microinclusions in these diamonds contain only HDFs, with no mineral microinclusions or microinclusions containing mixtures of HDF+mineral (Schrauder and Navon, 1994; Klein-BenDavid et al., 2007; Weiss et al., 2008; 2009). Thus their LA analyses solely represent the compositions of the trapped fluids.

Silicic HDFs reside in the Jwaneng diamonds, in single samples from DeBeers-Pool, Koingnaas and Kankan and in the inner parts of the two zoned diamonds from Kankan (see Weiss



et al., 2009 for further description). Low-Mg carbonatitic HDFs are found in the outer part of the two zoned diamonds from Kankan and in a single Diavik diamond. Saline HDFs were trapped in four of the Diavik samples, two of the DeBeers-Pool and one Koingnaas diamond.

RESULTS

The trapped HDFs in all diamonds are highly enriched with incompatible elements (Figure 1). The most incompatible ones (Cs-Pr) reach levels of a few hundred to a few thousand times the primitive-mantle values with patterns of diverse shapes. The most variable are K, Rb, Cs, Nb and Ta. The LILE elements (Ba, Th, U) commonly continue the pattern of the light REEs. In this range of incompatible elements, two patterns are distinguished. One is mostly flat with no significant anomalies and a moderate decrease of concentrations from the most incompatible elements toward the more compatible ones; the other has elevated Ba, U, Th and LREE, depleted Nb and Ta and in most cases, highly depleted alkalis. We designate the first pattern "Bench" for its smoother appearance; the second is named "Table" as it resembles a flat high surface, the levels of Ba, Th and U, that stands on high legs rising from the lower alkalis on the left and Nb and Ta on the right. The more compatible elements show greater similarity characterized by variable negative anomalies of Sr, Ti, Zr, Hf and Y relative to REE of similar compatibility. However, in most cases larger anomalies are observed in the HDFs of "Table" patterns.

The difference between the "Table" and "Bench" patterns can be best expressed by the ratios (La, Pr)/(Nb, Rb) vs. (U, Th)/(Rb, Nb) (Figure 2a). Ba is somewhat less appropriate among the LILE elements due to its larger diversity. Plotting Rb/Nb vs La/Nb separates between the two patterns as well: the HDFs with "Table" pattern exhibit positive correlation between the two ratios, steep in the low values and becoming moderate in the higher ones. Those with "Bench" patterns vary significantly in Rb/ Nb but have all low La/Nb ratios (Figure 2b). Most HDFs with "Table" patterns also have steeper, more fractionated REE patterns compared to the ones with "Bench" patterns, but this is not as consistent a feature as the above ratios.

DISCUSSION

The two incompatible element patterns, "Table" and "Bench" are not unique to the diamonds we studied. We recognize both in numerous microinclusions-bearing fibrous diamonds that were studied previously (Rege et al., 2005, 2010; Zedgenizov et al., 2007, 2009; Tomlinson et al., 2009; Araujo et al., 2009; McNeill1 et al., 2009; Klein-BenDavid et al., 2010). All reveal similar fractionated REE patterns with variable negative anomalies in Sr (except for the most saline HDFs), Zr, Hf, Ti and Y. Nonetheless, in these diamonds we have no constraints on the presence or absence of mineral microinclusions, which may affect the pattern. Hence, we chose not to use the literature data for the present study and omitted data for diamonds from Diavik and DeBeers Pool that carry mineral micro-inclusions (Klein-BenDavid et al., 2007; Weiss et al., 2008).

Both patterns are found in low-Mg carbonatitic to silicic and in saline HDFs (Figure 1). The similar signature of incompatible elements in diamond-forming fluids from different mantle localities, well separated in space and time, is fascinating. No less surprising is the persistence of "Table" and "Bench" patterns in HDFs of such diverse major-element compositions. The uniformity in time and space and the decoupling between major- and trace-elements are the two main features that we seek to explain either as a source effect, or as a result of post-source processes, or a combination of the two.





Figure 1: Primitive-mantle-normalized trace-element patterns of trapped HDFs in 15 diamonds from South Africa, Guinea and Canada._Silicic compositions are in red, carbonatitic in green and saline in blue.



Figure 2: Th/Nb (a) and Rb/Nb ratios vs. La/Nb ratio in HDFs with "Bench" and "Table" patterns.

The source of the "Bench" pattern

Elemental ratios such as Ba/Rb, K/U, Nb/ (La, U, Th) and Th/Rb are remarkably uniform in most MORBs and OIBs (Hofmann and White, 1983; Jochum et al., 1983; Hofmann et al., 1986). The Nb/(Th, U, La) ratios in HDFs with "Bench" patterns change little, are similar to MORB/OIB/ PM values and fall on the edge of the array formed by MORB-OIB-PM when plotting these ratios against the Nb concentrations (Figure 3). The depleted MORB mantle generates mostly N-MORBs with La/Gd<1 (Salters and Stracke, 2004); it cannot produce HDFs with "Bench" patterns having





Figure 3: Nb/La ratio vs. Nb concentrations of HDFs in "Bench" and "Table" patterns, global MORB and OIBs (Hofmann, 2003) and primitive mantle (PM, McDonough & Sun 1995).

La/Gd ratio of ~4-7 even at very small fractions of melting. Less depleted sources in the asthenosphere are inferred from the compositions of E-MORBs and OIBs. These are characterized by enriched incompatible-element patterns with moderate decrease in concentration from Cs to Lu and La/Gd ratios of \sim 3-6 (Eisele et al., 2002; White and Duncan., 1996; Wedepohl and Baumann, 1999), similar to HDFs with "Bench" patterns. In order to examine the formation of such HDFs by melting of a similar asthenospheric source, we calculated the compositions of peridotite (65% olivine, 28% orthopyroxene, 5% clinopyroxene and 2% garnet) in equilibrium with the silicic HDFs from Jwaneng and Koingnaas (Figure 4). Using 0.1% as the fraction of melting represented by the HDFs, the calculated sources lay between the range of PM and depleted MORB mantle (DMM) values for the



Figure 4: Calculated source compositions of silicic HDFs with "Bench" incompatible pattern. We used partition coefficients from Green (1994) and a mantle mineral mode of 65% olivine, 28% orthopyroxene, 5% clinopyroxene and 2% garnet for the calculations. The gray area represents the compositional range between primitive and depleted MORB mantle (DMM).

most incompatible elements (Cs-Sr); the more compatible elements are higher by 1.7 ± 0.9 compared to PM values. The similarity suggests that an asthenospheric source for the silicic HDFs with "Bench' pattern is possible.

The formation of the "Table" pattern

In HDFs with the more fractionated "Table" patterns the Nb/(Th, U, La) ratios deviate from the strict MORB/OIB/PM range and decrease by ~ 2 orders of magnitude with decreasing Nb content (Figure 3). Fractionation between adjacent incompatible elements, leading to strong negative anomalies in K, Rb, Cs, Nb and Ta, suggests the involvement of mica and Fe-Ti oxides in the formation of the "Table" pattern. PIC and MARID nodules consisting mainly of phlogopite, ilmenite, rutile, carbonate and clinopyroxene show a mirror-image of the negative anomalies characterizing the silicic and saline HDFs with "Table" pattern (Figure 5). The incompatibleelement patterns of PIC and MARID nodules are closely reproduced when calculating a source, consisting of 70% phlogopite, 8% ilmenite, 2% rutile, 7% carbonate and 13% clinopyroxene, in equilibrium with 0.1% partial melting of HDF with a "Table" incompatible-element pattern (Figure 5). The similarity suggests that these



Figure 5: Calculated source composition of silicic HDFs with "Table" incompatible pattern. We used partition coefficients from Sweeney et al. (1995) and Schmidt et al. (1999) for phlogopite, Zack & Brumm (1998) and Klemme et al. (2006) fot ilmenite, Low (1999) for carbonate, Klemme et al. (2005) for rutile and Green (1994) for clinopyroxene for the calculations.

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HDFs can be the residual melt left in PIC and MARID veins/rocks when they froze, or were derived by the melting of such a source.

Connecting "Bench" and "Table" patterns

We also examined possible relations between the "Bench" and "Table" patterns. Fractional crystallization of "Bench" to create "Table" patterns can be precluded. The majorelement constraints limit phlogopite removal to less than 20%, not enough to produce the high depletion in alkalis of the "Table" patterns. Percolation of melts with "Bench" patterns through metasomatised lithosphere that contains phlogopite carbonate, ilmenite and rutile as accessory phases and has the trace-element composition of cratonic garnet peridotites does lead to evolution of a "Table" pattern and is not expected to change the major elements.

The percolation scenario involves melting of an asthenospheric source to produce HDFs with "Bench" patterns. These HDFs migrate through a relatively large volume of asthenospheric rocks to produce a homogenous carbon isotopic signature. As they migrate into the lithosphere they can either retain their characteristics and be trapped in diamonds, or percolate through metasomatized lithosphere, interact with the accessory minerals and evolve into the "Table" pattern.

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