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Trace element compositions of diamond-forming fluids in Voorspoed diamonds

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Introduction

The Kaapvaal craton in Southern Africa provides unique opportunities for detailed examinations of thermal, magmatic and metasomatic processes in the subcontinental lithospheric mantle (SCLM). Identifying and characterizing the metasomatic episodes in time and space is a step toward understanding the geological history and evolution of the SCLM, the nature and origin of the involved fluids, as well as the mechanism of diamond formation. High-density fluids (HDFs) trapped as microinclusions in diamonds are main metasomatic agents that provide insight to these processes in the Earth's mantle. Here we present data for 14 fibrous, HDF-bearing diamonds from the Voorspoed mine in South Africa, that reflect multiple diamond-forming events in a cooling lithosphere.

The diamonds

Voorspoed fibrous diamonds reveal three populations that differ in their nitrogen aggregation. A group containing 11-30% B-centers, a group containing 5-16% B-centers, and a single diamond with undetectable B-centers (~100% A-centers). Eight coated diamonds from the second group present higher aggregation levels in their transparent octahedral cores (34-52% B-centers) compared to 5-16% in the microinclusion-bearing coats (Kempe et al., 2021).

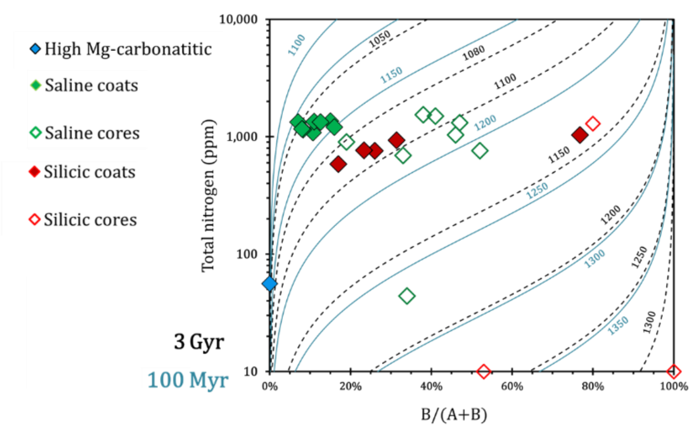

Figure 1: Nitrogen aggregation from A-centers to B-centers as a function of time (t) and temperature (T) for fibrous diamonds from Voorspoed. Isotherms are calculated for 100 Myr (turquoise lines) and 3 Gyr (black dashed lines).

The microinclusions

Voorspoed fibrous diamonds show a compositional variety of saline, silicic to low-Mg carbonatitic, and high-Mg carbonatitic HDFs. Although their compositions are overall similar to HDFs in other localities within the Kaapvaal craton, they exhibit some unique characteristics. Voorspoed saline HDFs (8 diamonds) are distinct by their lower K/Na and higher Cl/(K+Na) ratios. They also have among the highest Cl and FeO content (35-40 and 20-25 wt.%, respectively), and low MgO (<2 wt.%), similar to HDF in only a few other diamonds from the Ekati and Diavik mines in Canada and Koffiefontein and De Beers Pool mines in South Africa. The compositions of Voorspoed silicic to low-Mg carbonatitic HDFs (5 diamonds) are similar and fall within the silicic to low-Mg carbonatitic HDF compositional array. The high-Mg carbonatitic HDF from Voorspoed (1 diamond) is unique in its high K_2O content (31 wt.%). Nonetheless, the MgO and CaO content of ~18 wt.% each and low Cl content (2.2 wt.%) indicate its high-Mg carbonatitic nature (Kempe et al., 2021). The three HDF types fit the grouping based on the nitrogen aggregation state: the high-Mg carbonatitic diamond has 100% A-centers, the saline has 5-16% B-centers, and the silicic to low-Mg carbonatitic diamonds have 11-30% of their nitrogen in B-centers.

Trace element analysis of Voorspoed diamonds reveals elevated concentrations of incompatible elements relative to primitive mantle values (Fig. 2). The saline HDFs are mostly similar with high alkalis, Ba and LREEs compared to Th, U, Nb and Ta along with Sr, Ti and, to a lesser degree, Zr present varying negative anomalies relative to REEs of similar compatibility. These characteristics, especially the covariation of low Th, U, Nb and Ta and elevated alkalies are very similar to saline HDFs in diamonds from De Beers pool (Weiss et al., 2018), but differ from those in Finsch HDFs that are low in Ta and Nb, but show no depletion of Th and U (Weiss and Goldstein, 2018). The silicic HDFs in Voorspoed show larger variation in trace elements, some show relatively smooth patterns, while others show more fractionated patterns. There are some similarities to silicic HDFs in De Beers Pool and Koingnaas diamonds (Weiss et al., 2018). Th, U and Ba are elevated compared to the alkalis (K, Rb and Cs), while the negative anomaly of Ti is relatively small. Ta and Nb are both depleted compared to LREEs in both silicic and saline compositions. The carbonatitic HDF has a rather uniform pattern, except for elevated Hf and Zr.

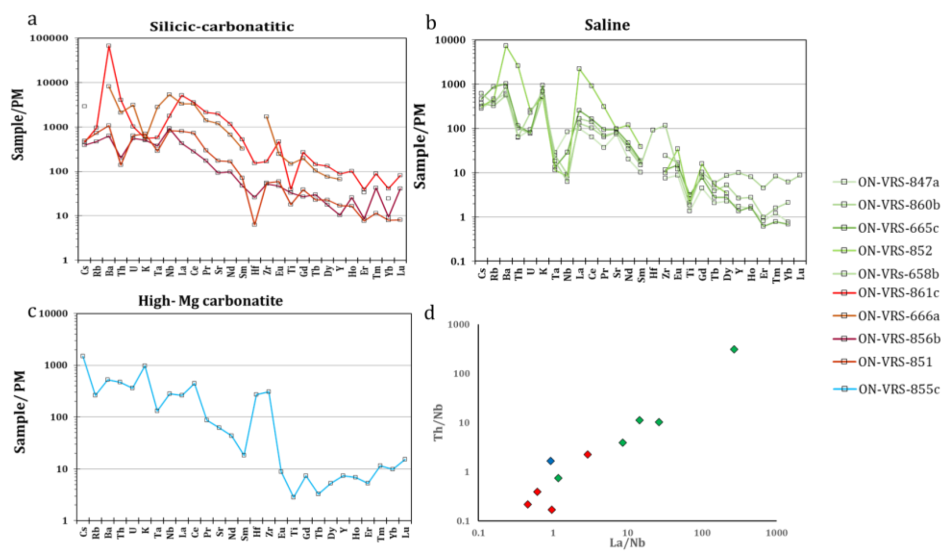

Figure 2: Trace elements of Voorspoed HDFs. a-c: Trace element abundance patterns of silicic, saline to low-Mg carbonatitic, and high-Mg carbonatitic HDFs, normalized to PM values and the concentration of K as determined by EPMA. d. Variation of Th and La relative to Nb, color-coded as in a-c.

Discussion

The distinct nitrogen aggregation of the fibrous diamond groups in Voorspoed and the lack of clear major or trace element evolutionary trends for each HDF type or intermediate compositions between the different types suggest different time-temperature formation histories. The full available record of aggregation data for diamonds from Voorspoed and the neighboring Lace mine, fibrous and non-fibrous monocrystalline diamonds (NFMC), includes three additional sets of data and reveals five distinct clusters that occupy distinct zones (labeled 1-5 in Fig. 3; Kempe et al., 2021).

High temperatures in Voorspoed lithosphere can be correlated with the eruption of the Ventersdorp flood basalts at the central Kaapvaal (ca. 2.7 Ga) or the Bushveld complex (ca. 2.06 Ga), and cooling rates of the lithosphere provide a time-temperature frame for the past ~2-3 Ga. Combining these data with the nitrogen aggregation systematics of fibrous and NFMC diamonds, we suggest that most Voorspoed diamonds formed during 5 metasomatic events: an old (or deep) event is hinted by the few diamonds with 100% B-centers, its timing cannot be constrained. Many iinclusion-bearing diamonds formed at 2-3 Gyr as a result of a major thermal perturbation, whereas the following three events occurred between 200-600 Myr, 30-90, and <30 Myr before kimberlite eruption. This sequence of events is implied by Voorspoed HDF compositional and nitrogen aggregation differences combined with the cooling of the lithosphere. It agrees with other occurrences in South Africa (e.g. Kimberley, Finsch and Koffiefontein) and may reflect thermal variation between the central and southwest Kaapvaal lithosphere.

The variation of La/Nb *vs.* Th/Nb is similar to the HDF trend from widespread localities (Fig.2; Weiss et al., 2022), with the silicic HDFs falling at low values, typical of 'Plained' patterns, and the saline with high ratios, similar to the 'Ribbed' ones, but with less pronounced anomalies. The lower Nb and Ti content in the saline fluid is likely due to the presence of accessory ilmenite and rutile (or other Fe-Ti minerals) that buffer these elements. The flatter patterns of the high-Mg carbonatitic diamond imply that residual titanate phases were not present and suggest higher temperatures and even shorter residence in the mantle, before the kimberlite eruption.

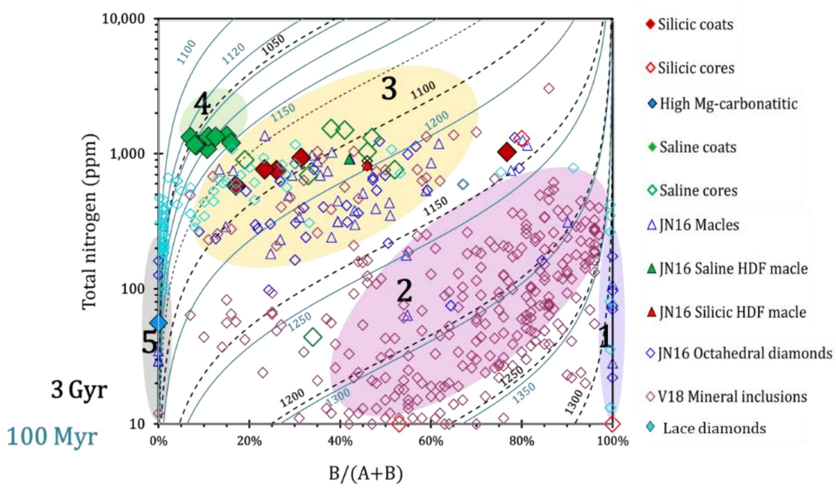

Figure 3: Five clusters, suggesting five diamond growth events in the lithosphere under Voorspoed area (Kempe et al., 2021). 1. Old and hot event leading to fully aggregated (~100% B-centers) in diamonds from Voorspoed and Lace (Jablon and Navon, 2016; Karaevangelou et al., 2022). 2. Most of the inclusion-bearing diamonds reported by Viljoen et al. (2018). 3. Most of the octahedra and macles from Voorspoed and Lace, the silicic fibrous diamonds and the saline cores. 4. The saline coats. 5. The carbonatitic diamond and diamonds from Lace.

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