11th International Kimberlite Conference Extended Abstract No. 11IKC-4544, 2017

Mineral inclusions in diamonds from Karowe Mine, Botswana: examining the mantle sources of a diamond population containing exceptionally large crystals.

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Introduction

Mineral inclusions in diamonds play a critical role in understanding the relationship between diamonds and mantle lithologies. Here we report the first major and trace element study of mineral inclusions in diamonds from the Karowe Mine (Orapa kimberlite cluster) in north-east Botswana, above the western edge of the Zimbabwe Craton. Our objective is to evaluate the mantle sources associated with a coarse diamond population containing very large gem-quality stones. From a total of 107 diamonds, 134 silicate, 14 oxide and 22 sulphide inclusions were recovered. Assigning the inclusions to principal suites, 55% of the diamonds classify as eclogitic (59 diamonds) and 43% peridotitic (46 diamonds). The remaining 2% consist of one sub-lithospheric diamond, containing a non-touching inclusion pair of majoritic garnet and omphacitic clinopyroxene, and a diamond of likely websteritic association.

Analytical Results

The 35 eclogitic garnets recovered classify into two groups on the basis of CaO content (Fig. 1): high-Ca garnets contain 7.04 to 16.10 wt% CaO and have ranges in Na_2O and TiO_2 between 0.13 to 0.55 wt% and 0.44 to 1.71 wt%, respectively. The low-Ca garnets range from 3.78 to 5.99 wt% CaO with Na_2O and TiO_2 contents vary between 0.07 and 0.24 wt% and 0.46 to 0.66 wt%, respectively. A total of 39 eclogitic clinopyroxene inclusions span the compositional range from (low-Cr) diopside-augite (n=16) to omphacite (n=24), based on their jadeite component (cut-off value of 0.2 for their molar 2Na/(2Na+Mg+Ca+Fe)). They contain variable Al_2O_3 (1.79-15.47 wt%), Na_2O (2.03-6.48 wt%), TiO2 (0.15-0.84 wt%) and low Cr_2O_3 (<0.27 wt%). A cation plot of Al vs Na shows common excess of Al over Na indicative of the presence of a Tschermaks component. In addition to the major eclogitic inclusions, three kyanites were recovered, two colourless and one deep blue. The latter coexisted with an orange garnet and had elevated levels of TiO_2 (0.31 wt%), Cr_2O_3 (0.17 wt%), FeO (0.34 wt%) and MgO (0.18wt%) compared to the two colourless kyanites where these oxides totalled <0.1wt%. The associated garnet contained 7.04 wt% CaO, which is too low for derivation for typical grospydite(value of >0.5 at molar calculation (Ca/Ca+Mg+Fe)). In 3 diamonds three pure SiO_2 inclusions were found and are assumed to represent primary coesite. They were separately associated with garnet, clinopyroxene and sulphide. The garnet belongs to the low-Ca group, the clinopyroxene to the low-Cr diopside-augite class and the sulphide has a low Cr content indicative of an eclogitic origin.

In the peridotitic suite, 38 olivine inclusions have Mg# 92.26 to 94.18 with a mean of 93.09 and a median of 93.11. On the basis of coexisting garnets or Mg-chromites (worldwide, with one exception, associated with lherzolitic inclusions), eight are harzburgitic. Based on their generally similar Mg# (mean of 93.02 and median of 93.10), the remaining olivines likely also are mainly of harzburgitic paragenesis. NiO contents in olivine vary between 0.25 and 0.39 wt% (mean of 0.37 and median of 0.36 wt%). Garnet inclusions are harzburgitic (n=8; Fig. 1) and lherzolitic (n=1), with Cr_2O_3 contents ranging between 5.65 and 14.70 wt% and CaO varying between 0.91 and 5.68 wt%. Four garnets have very low CaO contents (0.91-1.79 wt%), indicative of potentially dunitic sources. One of these low-Ca garnets is very rich in Cr_2O_3 (14.70 wt%; Fig. 1). All harzburgitic garnets record very low TiO_2 contents (<0.05 wt%) compared to a single lherzolitic garnet which has elevated TiO_2 (0.24 wt%).

The Cr_2O_3 contents of the 11 Mg-chromites were analysed, two coexisting with olivines, range between 61.83 and 67.28 wt% and TiO_2 varies between 0.06 and 1.12 wt%. All the chromites recorded more than 65.16 wt% Cr_2O_3 and less than 0.40 wt% TiO_2 content, except one with Cr_2O_3 of 61.83 wt% and a high TiO_2 at 1.12 wt%. The six orthopyroxene inclusions recovered have a narrow Mg# range (93.56-94.53; mean 94.00 and median of 94.04), CaO contents between 0.31 and 0.62 wt% and Al_2O_3 contents 0.53 to 0.98 wt%. Two of the orthopyroxenes coexist with garnets, one harzburgitic and one lherzolitic. Of the remaining four inclusions (one co-existing with olivine), two can be assigned to the harzburgitic paragenesis based on their high Mg# and low CaO content (see Fig. 14 of Stachel & Harris, 2008), the other two may be either lherzolitic or harzburgitic. The single Cr-diopside inclusion recovered has an Mg# of 93.11, a Cr_2O_3 content of 0.54 wt%, Na_2O at 0.29 wt% and Al_2O_3 at 0.67 wt%.

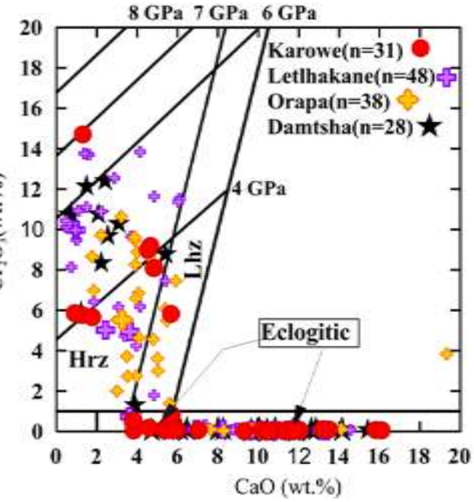

Figure 1: Cr_2O_3 vs CaO diagram for garnets from Karowe and other mines in Orapa cluster(Deines & Harris,2004;Stachel et al.,2004; Deines et al.,2009) Cr-in-garnets isobars are from Grütter et al.,2006.

The majoritic garnet in the sub-lithospheric diamond has 3.23 Si atoms per formula unit ([O]=12), accompanied by high Na_2O (0.76 wt%) and TiO_2 (1.43 wt%), and low CaO (4.60 wt%). The chemical composition of the accompanying clinopyroxene is omphacitic. A single orthopyroxene inclusion shows an exceptionally low Mg# (56.67), a very high CaO content (1.43 wt%) and elevated Al_2O_3 (0.93 wt%) and Cr_2O_3 (0.20 wt%) concentrations. Based on these characteristics the inclusion is tentatively assigned to the websteritic suite, but based on its very high CaO content could also be of sublithospheric origin.

Of the 22 sulphide inclusions recovered, 20 belong to the eclogitic suite based on low Cr contents (<0.03 at.%) and associated inclusion minerals. Only 5 inclusions consisted of monosulphide solid solution (mss), 2 associated with pentlandite and chalcopyrite respectively; 14 were pyrrhotites, of which three coexisted with pentlandite, chalcopyrite and pyrite separately and one with a pyrite-chalcopyrite assembly; 3 were pentlandites, one being associated with a Ni-Fe alloy. The mss has Ni contents of 7.33-13.79 at.%, and the pyrrhotites have a range in Ni from 0.12- 5.21 at.%. The alloy has a composition of 69.00 a.t% Ni, 29.38 at.% Fe and 1.51 a.t% Co. The two peridotitic sulphides are mss and contain 0.37 at.% Cr; they were both recovered from the same diamond along with an olivine.

Trace element concentrations were analysed for 12 garnets and 12 clinopyroxenes from the eclogitic suite. The low-Ca (n=3) garnets exhibit steep positive slopes within the $LREE_N$ and less positive ones at $MREE_N$-$HREE_N$, the latter at about 11 to 13 times chondritic abundances. Six of the high-Ca garnets show steep positive slopes within the $LREE_N$, but flat distributions between $MREE_N$ and $HREE_N$, The remaining three garnets are similar, except that they are slightly enriched in $LREE_N$. Of the 12 REE_N patterns for eclogitic clinopyroxenes, nine are characterized by a slight positive slope among the $LREE_N$ and a slight steady decline within $MREE_N$-$HREE_N$ from 10 to about 0.2 to 3 chondritic abundances. Two of the remaining clinopyroxenes have humped patterns, peaking in the $LREE_N$ at about 12 to 99 times chondritic abundances, but thereafter, their slopes are similar to the ones noted above. The last pattern has typical $LREE_N$ but is depleted in the $HREE_N$. This sample is the only one to show a positive Eu anomaly. Four garnet-clinopyroxene pairs from four diamonds were used to reconstruct eclogite bulk rock REE_N patterns (Fig. 2). They show broadly N-MORB like patterns with

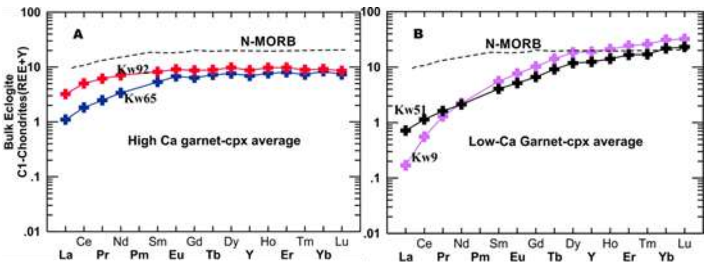

Figure 2: Reconstructed whole-rock REEN for eclogitic bulk rocks associated with high-and low-Ca garnets(assuming grt:cpx=1:1. N-MORB composition is from Sun & McDonough, 1989.

overall REE depletion for high-Ca garnet associated bulk rocks and prominent $LREE_N$ depletion for the low-Ca associated bulk rocks. Furthermore, five harzburgitic and one lherzolitic garnet were analysed. The harzburgitic garnets show distinctly sinusoidal REE_N patterns with strongly variable overall REE contents. The single analysed lherzolitic garnet has a normal REE_N pattern with flat $MREE_N$-$HREE_N$ at about 3 times chondritic abundance. The majoritic garnet shows a steep negative slope from $LREE_N$ (~100× chondritic) to $HREE_N$ (at about chondritic abundance)

Geothermobarometry

Non-touching garnet-orthopyroxene inclusion pairs (n=2) indicate peridotitic diamond formation at 1060 °C / 48.9 kbar and 1090 °C / 51.5 kbar, i.e. along a 38 mW/m^2 geothermal gradient. This value is slightly below the ~40 mW/m^2 paleogeotherm derived from mantle xenoliths at Letlhakane (Stiefenhofer et al., 1997). Cr-in-garnet barometry (Grütter et al., 2006) indicates peridotitic diamond formation up to a (minimum) depth of up to 220 km (Fig. 1). Based on Ca-in-opx thermometry, the presumed single websteritic pyroxene last equilibrated at 1380 °C, which suggests derivation from a thermally perturbed lithospheric source or from below the lithospheric mantle. Based on Si excess, the majoritic garnet inclusion derives from a depth of about 361 km.

Discussion and Conclusions

With few exceptions, the chemical composition of the eclogitic and peridotitic inclusions in Karowe diamonds compares well to previous studies on inclusion-bearing diamonds from other kimberlites in the Orapa cluster (Orapa, Damtshaa and Letlhakane mines). Among the eclogitic garnets, one sample records the highest TiO_2 concentration (1.71 wt%) yet observed in the Orapa cluster and the same garnet is aslo enriched in LREE and Zr (130 ppm). This indicates a higher metasomatic activity for Karowe eclogitic diamond sources. In the peridotitic garnets, one Karowe inclusion shows a much higher Cr_2O_3 content (14.70 wt%) than previously observed in the Orapa cluster, suggesting a very thick and highly depleted cratonic lithosphere at the time of diamond formation. Harzburgitic garnets are characterised by $LREE_N$ depletion, in contrast to $LREE_N$ enriched patterns for the bulk of Orapa harzburgitic garnets (Stachel et al., 2004). The sublithospheric inclusion suite reported here, consisting of a majorite garnet and possibly a Ca-rich orthopyroxene, is unique within the Orapa cluster and may provide a key link to the presence of exceptionally large diamonds at Karowe (Smith et al. 2017).

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