

Diamonds in the Kimberley area formed from mantle volatiles

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Introduction

Whether lithospheric (i.e. 150-250 km deep) eclogitic and peridotitic diamonds grew from isotopically-similar melt(s) and/or fluid(s) deriving from the convective asthenosphere is still a subject of debate. Some authors conclude that the ¹³C-depleted signature of eclogitic diamonds testifies to a subduction-related diamond formation whereas others have emphasised that they primarily derive from a mantle-derived source.

The present contribution addresses this question further using an unprecedented number of diamonds from the Kimberley Pool kimberlite cluster (28°45'S; 24°50'E) which includes the former five historical economic pipes Bultfontein, Dutoispan, De Beers, Kimberley and Wesselton. The first study on diamond characteristics (shape, color, size, luminescence) and paragenesis from individual kimberlitic pipes has shown that diamonds have the same source region and, accordingly, that the pipes have a same deep kimberlitic root (Harris et al., 1984). At the date of sampling, only three kimberlites, Bultfontein, Dutoispan and Wesselton were mined. As the productions being grouped, it is thus not possible to distinguish the pipe from which a diamond originated, thus the wording of *Kimberley Pool* or *DeBeers Pool*.

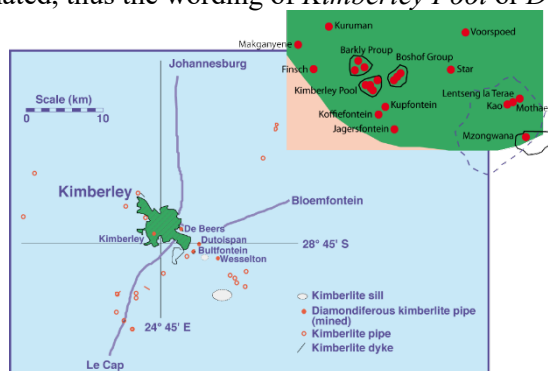


Figure 1 : Location of the different diamondiferous and non-diamondiferous kimberlites, sills and dikes composing the Kimberley Pool cluster. The five historical diamondiferous pipes are indicated and are contained within a circle of 8 km in diameter.

In this study, the C- and N- isotope compositions, N-contents and N-aggregation state of an unprecedented number of silicate- or sulfide-bearing diamonds has been carried out. Based on the type or chemical composition of silicate inclusions (Phillips et al., 2004), 225 samples comprising 43 eclogitic and 182 peridotitic diamonds were analyzed. Some peridotitic diamonds can be further classified into 83 and 20 diamonds belonging to the harzburgitic or lherzolitic permitting further discussion. In addition, 34 sulfide-bearing diamonds (33 eclogitic and one of mixed paragenesis, i.e. containing both peridotite and eclogitic sulfides) were analyzed, for C- and N- as well as for $\delta^{34}\text{S}$ and $\Delta^{33}\text{S}$ values of their inclusions.

Results.

$\delta^{13}\text{C}$ -values for harzburgitic diamonds vary from -6.90 to -3.90‰ and an extreme value down to -26.38‰ displayed by a zoned sample and a mean $\delta^{13}\text{C}$ -value is -6.22. Lherzolitic diamonds show $\delta^{13}\text{C}$ -values from -5.97 to -4.22‰ and a mean value of -5.13‰. Silicate-bearing eclogitic diamonds have $\delta^{13}\text{C}$ -values contained within a -15.38 to -3.06‰ interval, with a mean value of -5.70‰, and show a clear negative skewness. Sulfide-bearing eclogitic diamonds span a range from -6.34 to -4.82‰ with a mean value of -5.61‰. Strikingly, the different diamond populations show a $\delta^{13}\text{C}$ -mode which fall within a restricted range < 1‰.

Sixty-two of the 182 harzburgitic diamonds were classified as Type I with 51 allowing a $\delta^{15}\text{N}$ analysis. Figure 2 shows that $\delta^{15}\text{N}$ -values cover a range of ~20‰ from -12.3 to +8.1‰, with most of the data (i.e. 70%) being concentrated within a -6 to +3‰ interval. The mean $\delta^{15}\text{N}$ value is negative at about -0.3‰. Relative to previous studies, harzburgitic diamonds from Kimberley Pool showed more often positive (~54 %) than negative $\delta^{15}\text{N}$ -values. This distribution is also unique as the main mode of the $\delta^{15}\text{N}$ -distribution is centered around +1‰. It may be tempting, therefore, to suggest a bimodal distribution of harzburgitic $\delta^{15}\text{N}$ -values with a mode at ~-5‰ and a second around +1‰. Such a distinction is however not supported by distinct chemical composition of the enclosed inclusions or nitrogen aggregation states. It is worth mentioning that positive $\delta^{15}\text{N}$ -values displayed by harzburgitic diamonds are generally associated with lower nitrogen contents (e.g. < 350 ppm), with the reverse, higher nitrogen contents occur among diamonds with negative $\delta^{15}\text{N}$ -values. A single lherzolitic Type I diamond yielded a $\delta^{15}\text{N}$ -value of ~-3.1‰. As shown by Figure 2, with the exception of a few eclogitic diamonds having low (i.e. <-8‰) $\delta^{13}\text{C}$ -values, (silicate or sulfide-bearing) eclogitic and peridotitic diamonds cover nearly identical $\delta^{13}\text{C}$ - $\delta^{15}\text{N}$ fields

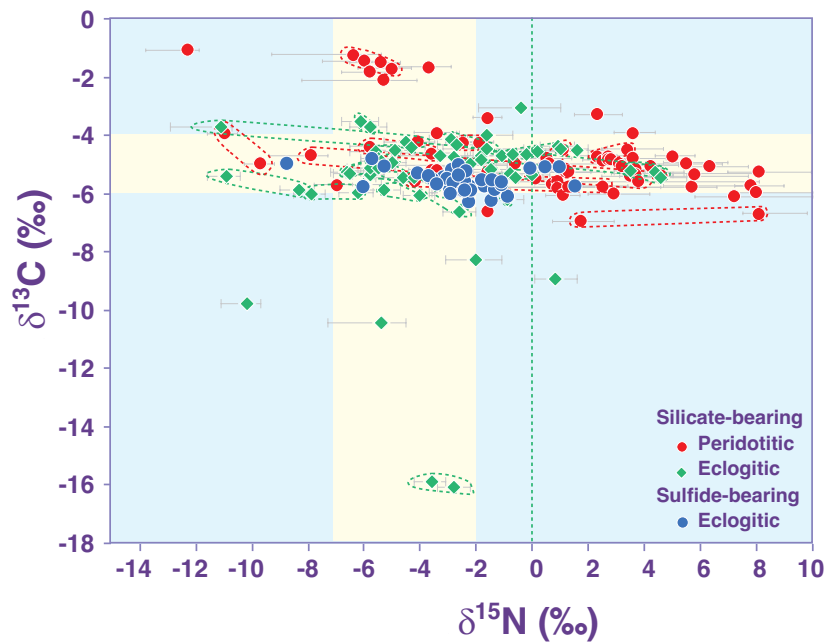


Figure 2 : $\delta^{13}\text{C}$ - $\delta^{15}\text{N}$ -values of silicate-bearing peridotitic, silicate-bearing eclogitic and sulfide-bearing eclogitic diamonds of Kimberley diamonds. The figure illustrates their striking overlap which implies that most diamonds, whatever their paragenesis, derive from a similar source of volatiles.

The sulfide-bearing diamonds cover a large range of $\delta^{34}\text{S}$ -values, from -1.8 to +6.1‰ and an extreme value at 11.4‰. Most inclusions have $\Delta^{33}\text{S}$ of 0.0 ± 0.2 ‰ yet two samples with positive $\Delta^{33}\text{S}$ up to 0.3‰.

Discussion

A unique Ib-IaA eclogitic diamond highlights a rare diamond population with a short mantle residence type (a few My) – this type of N-aggregation characteristics is inconsistent with a ~2.9 Gy mantle residence

time deduced for sulfide-bearing eclogitic diamonds (Richardson et al., 2001). The comparison of mantle equilibration temperatures deduced from infrared spectroscopy and inclusion studies highlights significant discrepancies. These observations suggest either that diamonds form over long time intervals or that certain impurities (such as H, Ni, Si) affect the activation value for N-aggregation, which should not be considered as a constant or strict value.

Carbon stable isotope compositions vary greatly from one (sub-)paragenesis to the other, with distinct range and skewness, yet the mode of each distribution fall within a range of 0.8‰, highlighting a main carbon source for both eclogitic and peridotitic diamonds. This conclusion is re-inforced by the coupled N-isotopes systematics showing striking overlap among peridotitic and eclogitic diamonds (Figure 2). These values are centered around the mantle value (at $\delta^{13}\text{C} \sim -5\text{‰}$ and $\delta^{15}\text{N} \sim -5\text{‰}$) and highlight that diamonds below Kimberley primarily derived from mantle-derived volatiles. Many studies suggested that the C- and/or N-isotope compositions deviating from mantle values should be interpreted as a result of mixing a mantle endmember with a low $\delta^{13}\text{C}$ recycled endmember. This model might provide an explanation for the positive $\delta^{15}\text{N}$ -values seen in >50% of peridotitic silicate-bearing diamonds. It is worth mentioning that eclogitic diamonds are dominated by mantle- $\delta^{15}\text{N}$ -values, best typified by eclogitic sulfide bearing diamonds having $\delta^{15}\text{N}$ of $-2.3 \pm 1.9\text{‰}$. Our data are however inconsistent with such a suggestion; the hypothetical recycled endmember should have a both a positive $\delta^{15}\text{N}$ -value and low N-content, yet have a mantle-like $\delta^{13}\text{C}$ -value. In the light of the present data, a model calling for N-isotope variability through fluid differentiation appears equally plausible. The most conclusive evidence for recycling is brought from the $\delta^{34}\text{S}$ -values, although the high $\delta^{34}\text{S}$ and the lack of resolvable $\Delta^{33}\text{S}$ -values for most samples would rather point to a Proterozoic rather than Archean recycled component; yet the mantle like C- and N-characteristics points to metasomatic diamond formation and a decoupling of sulfur from carbon and nitrogen (Thomassot et al., 2009).

Eclogitic sulfide-bearing diamonds from Kimberley show distinct features characterized by higher N-content, and little variable C- and N-isotope compositions compared to silicate-bearing eclogitic diamonds. This result supports not only previous evidence from Jwaneng eclogitic sulphides (Thomassot et al., 2009) but also Panda peridotitic sulphide-bearing diamonds (Cartigny et al., 2009) which outlined distinct isotope characteristics between silicate-bearing and sulphide-bearing diamonds of the same paragenesis. This suggests that eclogitic sulfide-bearing diamonds and eclogitic silicate-bearing diamonds either (i) crystallized at a distinct period of time or (ii) that the sulfide-bearing diamonds crystallized before the silicate-bearing diamonds, i.e. as outlined by the fact that their isotope characteristics are more homogeneous for the former - a suggestion that is however not consistent with the lower N aggregation of sulfide-bearing diamonds or (iii) that they crystallized from distinct fluids, possibly having distinct oxygen fugacities.

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