

Eclogitic, Peridotitic, Metamorphic Diamonds and the Problems of Carbon Recycling.

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Introduction

The origin of carbon in diamonds is still intensively discussed. About 20 years ago (Sobolev *et al.*, 1979), it was recognised that one type of diamond, referred as "eclogitic" (formally diamonds which contain silicate inclusions of eclogitic composition) cover a large range of $\delta^{13}\text{C}$ -values from -35 up to +3‰, as opposed to "peridotitic" diamonds and to other mantle products such as carbonates from kimberlites, MORB, OIB and carbonatites generally restricted to a $\delta^{13}\text{C}$ -interval of -10 to 0‰ (e.g. Javoy *et al.*, 1986). Because the $\delta^{13}\text{C}$ -range defined by carbon either in sediments or in meteorites is broadly similar to that of eclogitic diamonds, it has been suggested that eclogitic diamonds crystallised from sedimentary carbon recycled into the mantle, down to the diamond stability field or from a primordial and heterogeneous mantle carbon (e.g. Deines *et al.*, 1993). These hypotheses consider that the variations recorded in diamonds mostly reflect source effects. These neglect the fact that stable isotopes fractionate during geological processes. Carbon isotope fractionation is important even at mantle temperatures and can be enhanced by distillation effects (Javoy *et al.*, 1986; Galimov, 1991).

C and N isotopes in diamonds : previous results

In order to constrain the origin of diamond carbon, we are now including the analysis of diamond nitrogen and its isotopic composition. Nitrogen is the main diamond impurity, strongly bonded within carbon atoms. Nitrogen isotopes can bring strong constraints on the origin of diamonds, because sediments are characterised by positive $\delta^{15}\text{N}$ -values, evolving towards even more positive $\delta^{15}\text{N}$ -values with increasing metamorphism whereas mantle nitrogen is characterised by negative $\delta^{15}\text{N}$ (Javoy *et al.*, 1986; Cartigny *et al.*, 1997, 1998a).

This situation strongly contrasts with that of carbon, for which the mixture of the two sedimentary endmembers (carbonates and organic matter) can account for the whole diamond $\delta^{13}\text{C}$ -range. For nitrogen, there is a single sedimentary isotopic signature different of the mantle signature.

The $\delta^{13}\text{C}$ - $\delta^{15}\text{N}$ systematic in *octahedrally-shaped* diamonds was based on the study of unknown paragenesis samples (Boyd and Pillinger, 1994). Results clearly favoured the recycling model, since low $\delta^{13}\text{C}$ were associated with mostly positive $\delta^{15}\text{N}$. The first systematic study of eclogitic diamonds from Kimberley Pool, South Africa (Cartigny *et al.*, 1998a) gave an opposite point of view, most eclogitic diamonds, in particular the low $\delta^{13}\text{C}$ -diamonds being characterised by a negative $\delta^{15}\text{N}$. The subsequent study of Jwaneng eclogitic diamonds (Cartigny *et al.*, 1998b), by giving strictly negative $\delta^{15}\text{N}$ -values over the whole diamond $\delta^{13}\text{C}$ -range clearly supported a mantle-derived origin of the carbon and nitrogen of these diamonds. We pointed out that it was possible to account for the large diamond $\delta^{13}\text{C}$ -range of eclogitic diamonds and for a restricted $\delta^{13}\text{C}$ -range in peridotitic diamonds by a crystallisation from the same fluids, the evolution of these mantle fluids being different in an eclogitic and peridotitic environments. In an eclogite, it is actually possible that CO_2 loss (enriched in ^{13}C) leaves a ^{13}C depleted residue from which eclogitic diamonds can subsequently crystallise (Luth, 1993; Cartigny *et al.*, 1998b). Because this reaction cannot

occur in a peridotite over the temperature-pressure range from which most diamonds derived, peridotitic diamonds are likely to show rather constant $\delta^{13}\text{C}$ -values.

Thus, to date, eclogitic diamonds seem to be characterised by negative $\delta^{15}\text{N}$ -values and contrary to the suggestion of Boyd and Pillinger (1994), no mineralogically identified eclogitic diamonds with low $\delta^{13}\text{C}$ and high $\delta^{15}\text{N}$ -values have been reported.

The present study, where we compare new data obtained on eclogitic diamonds from Orapa, data on other eclogitic diamonds and data on metamorphic microdiamonds (analysed in collaboration with an other group (see DeCorte *et al.*, this volume)) shows that the presence of some eclogitic diamonds with high $\delta^{15}\text{N}$ (up to 7‰) and low $\delta^{13}\text{C}$ (down to -22‰) is, again, unlikely to characterise a direct formation from recycled organic material., and also shows that kimberlitic macrodiamonds are unlikely to derive from a virtual metasedimentary source typified by metamorphic microdiamonds.

Methods and results

Over the sample set from Orapa analysed by Deines *et al.* (1993), 15 eclogitic, 6 peridotitic and 6 websteritic new diamond chips were specifically selected for $\delta^{13}\text{C}$, $\delta^{15}\text{N}$ and nitrogen content determinations, on the basis of the $\delta^{13}\text{C}$ -values measured previously. Samples were analysed using the procedure described by Boyd *et al.* (1995). Eclogitic diamonds have $\delta^{13}\text{C}$ varying from -18.31 to -3.39‰ and a range, of course, similar to that defined by Deines *et al.* (1993). $\delta^{15}\text{N}$ range from -11.4‰ up to +6.4‰, and nitrogen concentrations from 1067 to 24 ppm. Eclogitic diamonds define a linear trend from $\delta^{13}\text{C} \approx -5‰$, negative $\delta^{15}\text{N}$ (-12 to -5‰) and high nitrogen concentrations towards more negative $\delta^{13}\text{C}$, down to -22‰, positive $\delta^{15}\text{N}$, up to +7‰ and lower nitrogen concentrations down to 0 ppm.

The 6 peridotitic diamonds we analysed have $\delta^{13}\text{C}$ -values ranging from -19.92 to -5.51‰, $\delta^{15}\text{N}$ from +19.6 to +2.5‰ and N contents from 411 to 25 ppm. 6 websteritic diamonds have $\delta^{13}\text{C}$ from -19.03 to -7.27‰, $\delta^{15}\text{N}$ from -12.8 to +15.6‰ and N contents from 548 to 24 ppm. Over the sample set, $\delta^{15}\text{N}$ and $\delta^{13}\text{C}$, $\delta^{15}\text{N}$ and N, $\delta^{13}\text{C}$ and N seem to vary independantly in both peridotitic and websteritic diamonds.

Discussion

For the first time, a single mine provide diamonds showing a continuity from a "mantle signature" (high $\delta^{13}\text{C}$ -negative $\delta^{15}\text{N}$) towards the field of low $\delta^{13}\text{C}$ diamonds (low $\delta^{13}\text{C}$ -positive $\delta^{15}\text{N}$ and thus with a "recycled" signature), allowing the origin of eclogitic diamonds with low $\delta^{13}\text{C}$ -values to be adressed on the basis of $\delta^{13}\text{C}$ - $\delta^{15}\text{N}$ -N variations.

The $\delta^{13}\text{C}$ - $\delta^{15}\text{N}$ covariations are unlikely to characterise mixing relationships. For this, we expect mixing hyperbolic curve in a $\delta^{13}\text{C}$ - $\delta^{15}\text{N}$ diagram and not the linear trend observed. The only way to observe such a linear trend would consist in mixing two endmembers with nearly identical C/N ratios (the mantle ratio is between 200 and 500). This is not the case, the ratio varying from 1000 to infinity. Ironically, the peridotitic and websteritic diamonds would be less incompatible with the "recycling" model.

In contrast, the linear trend defined by eclogitic diamond can be reconciled by considering a high temperature fractionation process. Following a Rayleigh distillation process, the equations governing the evolution of carbon and nitrogen isotopic compositions can be written as : $(\delta^{15}\text{N} - \delta^{15}\text{N}_0)/(\delta^{13}\text{C} - \delta^{13}\text{C}_0) = \Delta_N/\Delta_C \cdot (K_N - K_C)$. (with $\Delta = \delta_{\text{lost}} - \delta_{\text{growth medium}}$ and $K = C_{\text{lost}}/C_{\text{growth medium}}$, partition coefficient between the fraction extracted from the growth medium, either precipitated as a solid or lost in a more volatile rich fraction). In a $\delta^{13}\text{C}$ - $\delta^{15}\text{N}$ diagram, the evolution of mantle fluids defines a linear trend. During the differentiation of the mantle fluids, the growth medium is depleted in nitrogen, diamonds have thus lower N with decreasing $\delta^{13}\text{C}$ -values.

A further argument to support this view can be proposed by comparing $\delta^{13}\text{C}$ - $\delta^{15}\text{N}$ -N contents of (macro)diamonds from kimberlites and metamorphic (micro)diamonds from Kokchetav (see Sobolev and Shatsky, 1990). The origin of the carbon in microdiamonds is not yet fulfilled and the aim of the $\delta^{13}\text{C}$ - $\delta^{15}\text{N}$ study is to constrain its origin. Let us assuming for the purpose of this study, that metamorphic microdiamonds do trace a recycled component. Metamorphic microdiamonds have moderately low $\delta^{13}\text{C}$ -values (from -10 down to -15‰) and generally positive $\delta^{15}\text{N}$ -values (up to +10‰) with high N (from 800 to 3500 ppm). As a first approximation, metamorphic microdiamonds and macrodiamonds from Orapa are nearly identical from a $\delta^{13}\text{C}$ - $\delta^{15}\text{N}$ and it could be suggested they derived from a single source (i.e recycled metasediments). However, the trend from high N (about 1000 ppm) towards lower N (down to 0 ppm) with decreasing $\delta^{13}\text{C}$ and increasing $\delta^{15}\text{N}$ -values of macrodiamonds is incompatible with the observation that the positive $\delta^{15}\text{N}$ -values of metamorphic diamonds corresponds to very high (up to 3500 ppm) and not very low nitrogen concentrations.

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