

Microdiamonds from UHP metamorphic rocks of the Kokchetav massif and their bearing on carbon and nitrogen recycling

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A precise knowledge of the nature and the amount of the material recycled into the mantle is essential to place accurate constraints on the balance between atmosphere-crust and mantle systems. In particular, the amount of carbon and nitrogen possibly recycled into the mantle is difficult to estimate from direct observations, since most of light elements are lost, during subduction, through devolatilisation processes. To date, field observations of palaeo-subduction zones are mostly limited to amphibolite facies (e.g. Bebout and Fogel, 1992). Nitrogen being the main diamond impurity, analysing metamorphic microdiamonds from the Kokchetav massif, the only ultra-high pressure (UHP) massif in the world known to provide a significant amount of *in situ* formed microdiamonds, allows a direct observation of both carbon and nitrogen subducted at great depths and the metamorphic fluids produced at pressures greater than 40 kbars.

At the Kokchetav massif, microdiamonds have been described in different rock-types including garnet clinopyroxenites, garnet-clinopyroxene dolomitic rocks, gneiss and in the alluvial placers derived from the massif. Microdiamonds occur mainly as inclusions in garnet, clinopyroxene, zircon and in secondary mineral aggregates replacing garnet and clinopyroxene (e.g. Sobolev and Shatsky, 1990).

Method, samples and results

Alluvial microdiamonds and diamonds from garnet pyroxenites and dolomitic rocks have been analysed. Samples were mounted into platinum with a combustion apparatus slightly modified relative to more conventional macrodiamonds. Analytical preci-

sion for $\delta^{15}\text{N}$, N and $\delta^{13}\text{C}$ is about 0.5‰, 5% and 0.05‰ respectively. Nitrogen blanks were ~3 nanograms at $\delta^{15}\text{N}$ between -10 and +10‰. The rather big size (up to 500 micrometers) of alluvial diamonds allows a single stone to be analysed, whereas the small sample size of *in situ* diamonds (mean ~12 micrometers) does not. The latter diamonds were grouped in a ~0.5 milligram samples. Accordingly, only alluvial diamonds give access to the sample variability from one sample to another, *in situ* diamonds allowing only the mean $\delta^{13}\text{C}$ - $\delta^{15}\text{N}$ -N to be obtained. *In situ* diamonds from garnet clinopyroxenites and dolomitic rocks were analysed

In contrast with alluvial diamonds, diamonds from clinopyroxenite and dolomitic rock never give the theoretical yield. This reflects the presence of inclusions within diamonds, as identified on the basis of FTIR spectroscopy of the same diamonds by De Corte *et al.* (1998). It is crucial to emphasise this is (obviously) not the consequence of a bad sample purification and cleaning. After thermochemical extraction, the diamond fraction contains next to diamonds, zircons and more rarely garnets or rutiles. Handpicking was performed to purify samples, resulting to a negligible zircon content. Nitrogen content of diamonds from clinopyroxenite and dolomitic rocks were calculated assuming that all the nitrogen was initially present within the diamond.

Alluvial diamonds show rather low $\delta^{13}\text{C}$ -values, from -15.92 to -10.57‰, $\delta^{15}\text{N}$ from -0.8 to +1.1‰ and high N-contents, from 2324 to 3643 ppm. Different analyses of diamonds from clinopyroxenite and from carbonates gave, of course, identical results, within the experimental error. The mean

$\delta^{13}\text{C}$ of diamonds from pyroxenites is -10.50% with a mean $\delta^{15}\text{N}$ of $+5.9\%$ and a very high N content of (av) 11143 ppm. Diamonds from carbonates give a mean $\delta^{13}\text{C}$ of -10.19% , with a mean $\delta^{15}\text{N}$ of $+8.5\%$ and N-content of 2462 ppm

Discussion

In situ and alluvial microdiamonds have clearly different mean $\delta^{15}\text{N}$ -values and N-content from one rock-type to the other, alluvial diamonds being characterised by slightly negative $\delta^{15}\text{N}$, while diamonds from dolomitic and clinopyroxenite rocks are enriched in ^{15}N by 5 and 10‰ respectively relative to air. These differences are strengthened by slight but significantly different mean $\delta^{13}\text{C}$ -values, -13.1% for alluvials, -10.5% for pyroxenites, and -10.2% for dolomitic rocks. The present data set gives thus a new evidence that at Kokchetav, different diamond subpopulations, linked to the host-rocks, can be identified, confirming previous suggestions (Sobolev and Schatsky, 1990; De Corte *et al.*, 1998).

The high nitrogen content of *in situ* diamonds from clinopyroxenites, above 10000 ppm, has to be compared with the highest value of 3000 ppm contained within the same diamonds as determined by FTIR spectroscopy (De Corte *et al.*, 1998). This large difference demonstrates that about 7000 ppm nitrogen are likely to be contained, as fluid inclusions (i.e. undetectable by FTIR). Together with carbonates and water inclusions, the presence of nitrogen fluid inclusions trapped during crystallisation calls for a diamond

formation, at least within garnet clinopyroxenites, from a fluid phase, as previously suggested by De Corte *et al.* (1998). Diamonds from carbonates are also likely to contain a significant amount of nitrogen, at least 1000 ppm, as fluid inclusions.

The absence of systematic covariations between the different diamond subpopulations does not support the idea of a diamond formation from a single source evolving, for example, through a Rayleigh distillation-type process. This suggests a limited mobility of the fluids associated with diamond growth, and make therefore the different metamorphic host-rocks the most plausible sources. However, it is unclear whether the negative $\delta^{15}\text{N}$ -values found in diamonds from alluvials could characterise a slight mantle contribution.

The results on metamorphic microdiamonds from the Kokchetav massif suggest that the burial of sedimentary carbon and nitrogen down to the diamond stability field is conceivable. The isotopic composition of subducted metasedimentary nitrogen is mostly positive, that of carbon is rather low with $\delta^{13}\text{C} \sim -10\%$ and C/N between 90 and 400.

References

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