

## C and N isotope compositions of diamonds from the calc-alkaline lamprophyres of Wawa (Superior Craton)

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### Introduction

Diamonds from the calc-alkaline lamprophyres of Wawa are unique in several aspects and have been object of detailed studies in the recent years (e.g. De Stefano et al., 2006; Stachel et al., 2006). The peculiarities of this diamond suite include the ancient age of the host rocks (2.7 Ga, Wyman and Kerrich, 1993), the occurrence in an orogenic setting, the predominance of red-orange and yellow cathodoluminescence colours, the presence of peridotitic and eclogitic syngenetic mineral inclusions within the same diamond, and a disequilibrium between mineral inclusions and its diamond host (De Stefano et al., 2006).

We conducted a combined study of stable isotopes of carbon and nitrogen in 13 diamonds from Wawa, while analyzing carbon isotopes alone in 48 other stones from the same suite. The intent is to test the hypotheses that have been proposed so far on the genesis of diamonds in this area (De Stefano et al., 2006; Stachel et al., 2006) and to characterize the source of carbon and nitrogen from which diamonds originated.

### Results

Sixty out of 61 of the studied diamonds from Wawa have  $\delta^{13}\text{C}$  values comprised between -5.3 and -0.74‰, and only one diamond falls out of this range showing a  $\delta^{13}\text{C}$  of -26.2‰ (mean=-3.0, mode=-2, Fig. 1). Out of 13 diamonds analyzed for  $\delta^{15}\text{N}$ , 10 show positive values ranging between 0.7 and 14.7‰, whereas the remaining have negative values at -17.6, 4.2, and -1.7‰ (mean=2, modes=9 and 1). No linear correlation is seen between the  $\delta^{13}\text{C}$  and  $\delta^{15}\text{N}$  values in the samples on which the combined isotopic study was conducted, although a general trend of decreasing  $\delta^{13}\text{C}$  with increasing N is observed (Fig. 4).

### Discussion

The C isotopic composition of diamonds from Wawa points clearly towards a mantle origin.

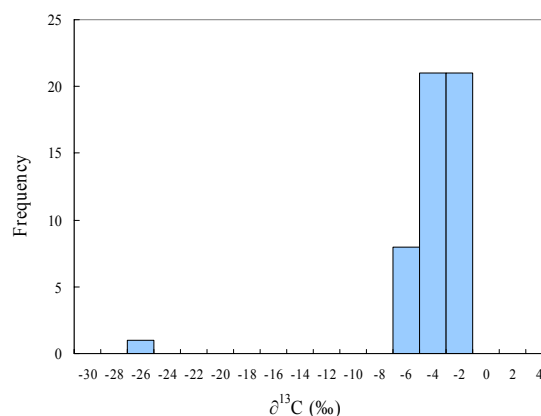


Fig. 1. Histogram showing the C isotopic composition of Wawa diamonds. Number of analyses=61.

Sixty samples out of the 61 studied display  $\delta^{13}\text{C}$  values that are close to -5‰, the value now universally accepted as typical of mantle derived carbon (e.g. Cartigny et al., 1998). The mean of -2‰ shows that these diamonds are slightly enriched in  $^{13}\text{C}$  with respect to the average mantle value, a feature that was also reported by Stachel et al. (2006) in a recent study on diamonds from the Wawa area. However, one sample shows a light isotopic composition ( $\delta^{13}\text{C}=-26.2$ ‰) similar to the average value of organic matter in marine sediments ( $\sim -25$ ‰, e.g. Cartigny et al., 1998). Most of the Wawa diamonds that were analyzed for their N isotopic composition (10 out of 13) yielded positive  $\delta^{15}\text{N}$  values, which resemble those of subduction related metasediments and metamorphic diamonds found in UHP terrains (Fig. 2 and 3), while the expected  $\delta^{15}\text{N}$  value of nitrogen in the mantle is -5‰ (Cartigny et al., 1998). Positive  $\delta^{15}\text{N}$  values are also quite common in peridotitic diamonds (Fig. 3), and Wawa diamonds by combined  $\delta^{15}\text{N}$  -  $\delta^{13}\text{C}$  values resemble peridotitic diamonds from other localities worldwide, whereas little to no overlap occurs with the fields of eclogitic, metamorphic and fibrous diamonds (Fig. 2). On average, though, Wawa diamonds tend to have slightly higher values of  $\delta^{15}\text{N}$  with respect to other peridotitic diamond suites (Fig. 2 and 3). A combination of “mantle” C isotopic signature with “crustal” composition of N in Wawa diamonds requires an explanation.

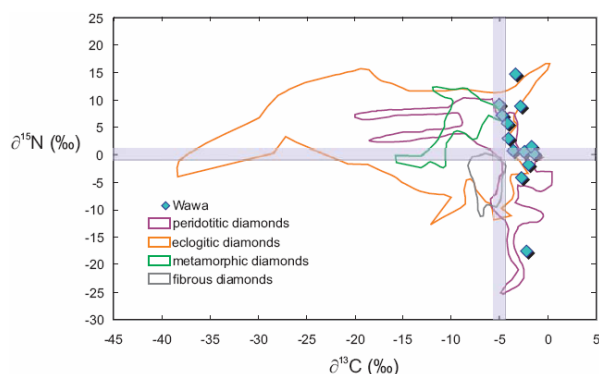


Fig. 2.  $\delta^{15}\text{N}$  versus  $\delta^{13}\text{C}$  plot showing the isotopic composition of diamonds on which the combined study was conducted. Number of analyses=13. Fields from diamonds worldwide are shown for comparison. Grey bands indicate the typical mantle values for  $\delta^{15}\text{N}$  and  $\delta^{13}\text{C}$  (e.g. Cartigny et al., 1998).

Formation of diamonds from the mantle and subducted crustal protoliths would account for the mixing of two sources. This model is supported by a study of syngenetic diamond inclusions in the Wawa diamonds (De Stefano et al. 2006). The diamonds belong to peridotitic and less abundant eclogitic parageneses. Occurrence of mineral inclusions from different parageneses within the same diamond suggests a small scale mixing between subducted oceanic crust and the mantle. Carbon isotopic signatures of the Wawa diamonds, however, is purely mantle-like (Fig. 1 and Stachel et al., 2006), and it is difficult to imagine that every single diamond would be made from “mantle” carbon, but “crustal” nitrogen. Also in contrast with the model of a mixed source is the fact that no linear trends of decreasing N content with increasing  $\delta^{13}\text{C}$  are seen in the plot of Fig. 4 for the studied diamonds. Such a trend would show the evolution of the source from a crustal end-member (with high N content and “organic”  $\delta^{13}\text{C}$  of  $-25\text{‰}$ ) towards a mantle end-member (with low N content and  $\delta^{13}\text{C}$  of  $\sim -5\text{‰}$ ).

One of the possible alternative explanations for the C and N isotopic signatures of Wawa diamonds is the heterogeneity of the source in the Archean mantle at the time of the diamond formation. This model would explain the difference between the Wawa diamonds and the population of fibrous diamonds worldwide (Fig. 2). Fibrous diamonds, being younger in age ( $<500$  Ma, e.g. Cartigny et al., 1997), would not bear the evidence of such “isotopic anomaly” in the Archean mantle, as older Wawa diamonds, or peridotitic diamonds in general. One would, however, expect the Wawa diamonds to show lower  $\delta^{15}\text{N}$  values than fibrous diamonds, as recycling of heavy crustal nitrogen into the mantle occurred continuously since the Archean (Cartigny et al., 1998; Javoy et al., 1998). In contrast to this, fibrous diamonds yield lower  $\delta^{15}\text{N}$  values than Archean diamonds from Wawa and peridotitic sources (Fig. 2). Moreover, the C isotopic signature of Wawa diamonds indicates a typical homogeneous mantle domain; almost all  $\delta^{13}\text{C}$  values from this study (60 out of 61) and from Stachel et al. (2006) (40 analyses in total) fall within an interval between  $-1$  and  $-6\text{‰}$ . In other words, it is not clear why the compositional heterogeneity in the mantle would appear exclusively in nitrogen isotopes.

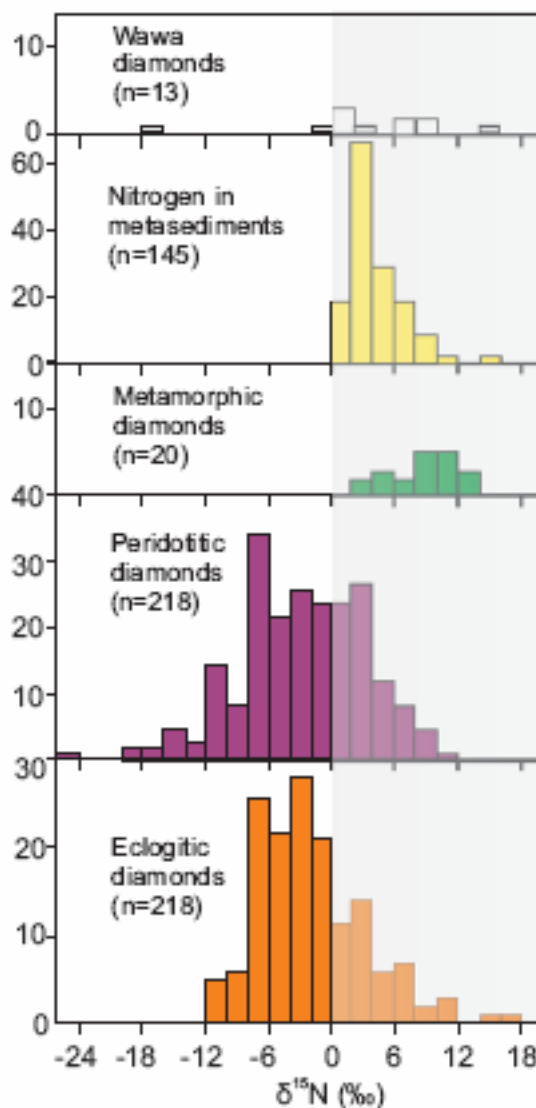


Fig. 3. Histograms showing the N isotopic compositions of diamonds from Wawa compared with subduction related metasediments and diamonds worldwide, and their relative abundances (modified from Cartigny, 2005).

Finally, another model explaining the origin of Wawa diamonds could involve metasomatism from a mantle fluid or melt. Metasomatic origin of diamonds is a widely accepted paradigm now, supported by multiple lines of evidence (e.g. Taylor et al. 1998; Stachel et al. 2004). This process, however, could not involve nitrogen isotopic fractionation in the mantle, as the Wawa diamonds with positive  $\delta^{15}\text{N}$  are also characterized by higher N contents, as is the case in diamonds from Namibia (Cartigny et al., 2004). Therefore, we propose that the metasomatic agent responsible for the formation of Wawa diamonds may have mobilized a preexistent recycled nitrogen reservoir stored in the mantle. This model would be consistent both with the mantle C isotopic signature of the Wawa diamonds and the predominant peridotitic inclusion paragenesis.

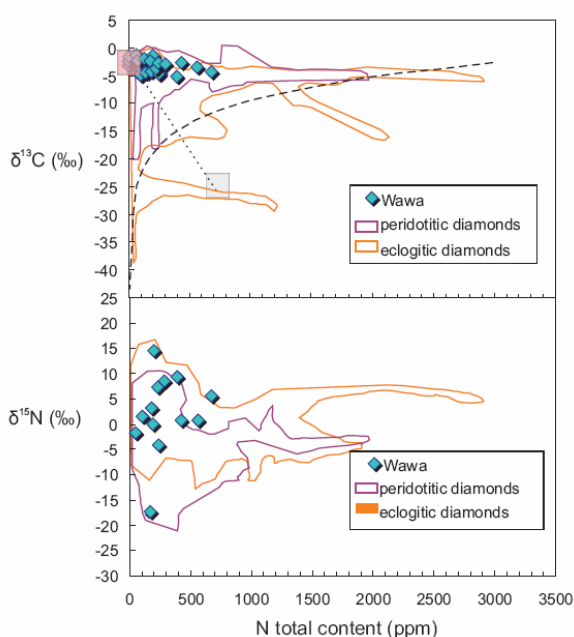


Fig. 4.  $\delta^{13}\text{C}$  vs N content and  $\delta^{15}\text{N}$  vs N content plots for Wawa diamonds. Number of analyses=44, for the upper plot; 13 for the lower one. Dashed curve indicates the “limit sector” where ~90% of worldwide diamonds fall (Cartigny, 2001).. Dotted line indicates a mixing trend between a hypothetical crustal end member (grey box) and a mantle end member (pink box).

## Conclusions

The studied Wawa diamonds show a series of typical mantle features including their C isotope compositions, N content and speciation, which are consistent with their peridotitic and eclogitic mineral inclusion chemistry. The studied Wawa diamonds by N and C isotopic compositions resemble peridotitic diamonds worldwide, but, on average, show higher positive  $\delta^{15}\text{N}$  values. We propose that Wawa diamonds formed through a metasomatic process induced by a mantle related fluid or melt. The processes that created Wawa diamonds were likely active in formation of peridotitic diamonds elsewhere.

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