

## Sulfide-bearing diamonds: The exception, not the rule

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The paradox between the low sulfide content of mantle xenoliths (about 300 ppmS) and the overabundance of sulfide minerals entrapped in diamonds (70% of inclusions) points to a possible genetic link between these two minerals. Traditionally, sulfide-bearing diamonds are thought to have an equivalent origin to other gem diamonds. Geochemical measurements from sulfide-bearing diamonds including dating using the Re-Os chronometer have been used to constrain the history of whole suites of diamonds (assuming that all gem diamonds would be comparable).

In order to test this assumption, we have undertaken a detailed geochemical study of 113 sulfide-bearing diamonds recovered from 3 different diamondiferous pipes from the Kaapvaal craton, Jwaneng (Botswana), Kimberley Pool and Koffiefontein (South Africa). We measured the N-content and aggregation state of 134 diamond chips, by IR spectroscopy. Each fragment has then been characterized with respect to their C- and N-isotopic compositions.

Sulfide bearing diamonds are N-richer (800 at.ppm in average) than other silicate-bearing diamonds from the same mine, yet the nitrogen aggregation state, which reflects the efficiency of diffusion through the crystal, is limited to a maximum of only 12% of Type IaB). The diamonds also display a narrow range of  $\delta^{13}\text{C}$  (from -8.4 to -3.1 ‰, st. dev. 1.5‰, excluding a single extreme value at -18.7‰). Associated  $\delta^{15}\text{N}$  values range from -13.6 to 8.3 ‰, have a normal distribution and a median value of -5‰.

The C- and N-isotopic compositions of sulfide-bearing diamonds are typical for a mantle reservoir and, *a priori*, their carbon source does not differ from those of other diamonds. The narrow range of  $\delta^{13}\text{C}$  values, however, is surprising and unexpected being characteristic of a rapid crystallization history, which is consistent with the high N-contents. More tellingly the low aggregation state is only compatible with a low temperature crystallization ( $T < 1000$  °C).

We conclude that sulfide-bearing diamonds represent a distinct diamond population that formed rapidly in a relatively low temperature environment. Consequently, conclusions based on these specific diamonds (e.g. Re/Os ages) may not apply to other diamonds, even from the same mines.

## Is there a common drive for the negative excursion of organic Carbon and the attenuated mass- independent-Sulfur at 2.7 Ga?

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In order to bring further insights into the prevailing environmental conditions during the  $\delta^{13}\text{C}$  negative Fortescue Excursion attributed to an increase in methanotrophic biomass, we carried out a detailed carbon ( $^{12}\text{C}$ ,  $^{13}\text{C}$ ) and multiple sulfur ( $^{32}\text{S}$ ,  $^{33}\text{S}$ ,  $^{34}\text{S}$ ,  $^{36}\text{S}$ ) isotopic study through the entire pristine core drilled from the slightly metamorphosed 2.7 Ga Tumbiana Formation.

Organic  $\delta^{13}\text{C}_{\text{PDB}}$  values vary markedly at meter scale and display a bimodal distribution with two maxima at -43 and -34‰. This isotopic record, together with petrological and other geochemical proxies, cannot be explained by secondary processes such as diagenesis or metamorphism but likely reflects variable contributions of  $^{13}\text{C}$ -depleted methanotrophic biomass to the organic matter. Sedimentary pyrites display Mass-Independent-Fractionation of sulfur isotopes (MIF-S) with  $\Delta^{33}\text{S}_{\text{CDT}}$  anomalies ranging between -0.24 and 1.64‰ (average 0.46‰) and show a linear relationship between  $\Delta^{33}\text{S}_{\text{py}}$  and  $\Delta^{36}\text{S}_{\text{py}}$  with a  $\Delta^{36}\text{S}/\Delta^{33}\text{S}$  ratio  $\sim -1.5$ , similar to that of most Mesoarchean rocks and probably related to changes in atmospheric composition (e.g.  $\text{CH}_4/\text{CO}_2$  ratio). Recognition of positive correlation between the  $^{12}\text{C}$ -enrichment of organic matter and MIF-S suggests a genetic link between the  $\delta^{13}\text{C}$  negative excursion and the observed increasing MIF-S fractionation of Late Archean rocks.

We propose that different types of metabolisms operating under various redox conditions were present in the Tumbiana paleo-environment and we suggest that the  $\delta^{13}\text{C}$  negative Fortescue Excursion would reflect biotic methane assimilation which leads to a conjoint decrease in atmospheric methane concentration and transient increase in MIF-S fractionation before the Great Oxidation Event.