Mystery of the volcanic mass-independent sulfur isotope fractionation signature in the antarctic ice-core

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We provide the first quantitative explanation for the observed record of sulfur mass-independent fractionation (MIF) in the Antarctic sulfates from the 1991 eruption of Mt. Pinatubo. Discovery of MIF in sulfur isotopes in the Archean/Early Proterozoic sediments and lack of MIF in sulfur in the younger rocks placed a strict upper constraint on the amount of oxidants and oxygen in the ancient Earth’s atmosphere prior to 2.3 Gyr ago. However, recent measurements in ice cores suggest that some non-zero MIF in sulfate can be delivered to Antarctica following large volcanic eruptions. Current photochemical experiments do not identify the specific reaction responsible for sulfur MIF production. Here we show that a time-dependent non-zero sulfur MIF can be delivered to the ground in the present atmosphere if the primary MIF producing process is SO$_3$ photolysis. Such photolysis has not been considered before, but is consistent with the available experimental data.

Coupled isotopic study ($\delta^{33}$S, $\delta^{34}$S, $\delta^{15}$N, $\delta^{13}$C) of sulfide-bearing diamonds (Jwaneng, Botswana)

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In order to better constrain the occurrence and the magnitude of mass independently fractionated sulfur in the mantle, we have undertaken to measure the multiple sulfur isotopes in sulfide inclusion-bearing diamonds coupled with C- and N-isotopes, N-contents and the nitrogen aggregation state of their host diamond. 54 octahedral diamonds from the Jwaneng kimberlite in Botswana, were examined.

We extracted and analysed 36 sulfides, 34 being Ni poor (<12wt%) and consisting of co-existing phases such as pyrrhotite, pentlandite and chalcopyrite typical of the eclogitic suite. Two inclusions showed high (>16wt%) and homogeneous Ni contents and are monosulfide solid solutions (MSS) typical of the peridotitic pargenesis. $\delta^{13}$C range from $-8.4\%$ to $-3.1\%$ with a single extreme value at $-18.7\%$ (median $\sim -5.4\%$). This tight distribution differs from that established on silicate-bearing diamonds from the same mine (median $\sim -10.3\%$ and a larger range of values).

$\delta^{15}$N range from $-13.2\%$ to $+8.3\%$ with an average of $-4.6\%$ (61% between $-8\%$ and $-2\%$). The diamonds are nitrogen-rich (average $\sim$780 ppm) and show low aggregation states (40% are pure IaA diamonds) compared to others Jwaneng silicate bearing-diamonds. All these results show that (1) sulfide bearing-diamonds represent a specific diamond group and (2) that they point to a mantle-related (i.e. not subduction-related) diamond formation.

$\delta^{33}$S, $\delta^{34}$S $\Delta^{33}$S were measured by secondary ion mass spectrometry using the CRPG IMS 1270 facility operating on multi-collection mode. Two sigma uncertainties are better than $\pm 0.2\%$ for single $\Delta^{33}$S measurement.

Available data on eclogitic diamond ($n = 9$) show significant and strictly positive $\Delta^{33}$S (up to 0.7 ‰). In contrast, the single peridotitic sulfide measured to date, shows a $\Delta^{33}$S close to zero. Values will be duplicated and extended to the entire sample set and the results presented and discussed at the conference.