Negative sulfur-MIF anomalies in metasomatized eclogites from Siberia

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Sulfur Mass Independent Fractionations (S-MIF), likely formed in the Archean atmosphere, are preserved in sedimentary rocks formed prior to 2.5 Ga [1]. Their recyclage into the mantle has been identified in metasedimentary sulfides included in diamonds, which carry significant S-MIF [2, 3]. However in both metasediments and diamond inclusions, most S-MIF values (carried by insoluble S-species) are positive, whereas the material balance of sulfur cycled from Archean atmosphere to sedimentary reservoirs requires that the average of all S-MIF is 0. Despite this requirement, the record of a negative S-MIF reservoir (likely dissolved in the oceans) is mostly absent, with only barite and sulfide of hydrothermal origin having these characteristics but representing a quite modest reservoir in size. Here we present a detailed petrological study coupled with *in situ* S-isotope measurements in 4 sulfides (~500μm in diameter) extracted from a mantle eclogite xenolith from the Mir kimberlite (Siberia). They consist of complex assemblages of (1) classic mantle sulfides (intergrowths of pyrrhotite and pentlandite) with (2) K-rich sulfides (djerfisherite) invaded by (3) veinlets of alteration-related minerals (mainly chlorite), resulting from multi-stage metasomatic processes [4]. Because of this complexity, we performed *in situ* multiple S-isotope measurements using a new Caméca ims 1280-HR2, allowing precise measurement with a spatial resolution < 20 μm, with precision for $\Delta^{33}S$ better than ±0.1 ‰.

Despite mineralogical heterogeneities, $\delta^{34}S$ in each sulfide has a narrow range (± 0.9 ‰). Most suprisingly, they show significant, exclusively negative MIF, ranging from 0 to -0.42‰ (±0.1 ‰, n=18). Metasomatic djerfischerite rims show smaller isotopic anomalies which cannot be clearly distinguished outside of uncertainty. We interpret the negative $\Delta^{33}S$ in the primary sulfides as reflecting an imprint of hydrothermal circulation in Archean oceanic crust. The smaller anomalies in the rims may reflect later reequilibration during modal metasomatism. Hence the signature appears to be evidence of a more widespread reservoir with negative $\Delta^{33}S$ that may balance the Archean S-MIF budget. The new S isotope data also provide further support for subducted oceanic crust as the protoliths of Siberian eclogites.

[1] Farquhar *et al.* (2000). [2] Farquhar *et al.* (2002). [3] Thomassot *et al.* (2007). [3] Misra *et al.* (2004).

Extreme ^{15}N-enrichments in 2.72-Gyr-old sediments: Evidence for a turning point in the nitrogen cycle

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Although nitrogen is a key element in organic molecules such as nucleic acids and proteins, the timing of the emergence of its modern biogeochemical cycle is poorly known. Recent studies suggests the establishment of a complete aerobic N biogeochemical cycle at about 2.68 Gyr. Here, we report new bulk nitrogen isotope data for the 2.72 billion-year-old sedimentary succession of the Tumbiana Formation (Pilbara Craton, Western Australia). The nitrogen isotopic compositions vary widely from +8.6‰ up to +50.4‰ and are inversely correlated with the very low $\delta^{13}C$ values of associated organic matter defining the Fortescue excursion (down to about -56‰).

We argue that the main driver of this exceptional high $\delta^{15}N$ values is the isotope fractionation associated with microbial ammonia oxidation, the produced nitrite and nitrate being totally converted to gaseous N_2O or N_2 by denitrification. The expression of this isotope fractionation in the rock record suggests that a small increase in oxidant availability allowed water column colonization by ammonia oxidizing micro-organisms, but was too limited to allow ammonium to be fully used up. The subsequent decrease of $\delta^{15}N$ values down to modern values 5 ±3‰ by 2.6 Gyr probably reflects a redox increase of at least part of the water column, leading to the establishment of a chemocline interface (localized either in the water column or in the sediment) where ammonium is quantitatively oxidized by denitrification as in modern environments. This study allows us to date precisely the onset of the oxidative part of the nitrogen cycle at 2.72 Gyr. We see the first evidence for ammonium oxidation, nitrification, and denitrification, which implies an increase in the availability of electron acceptors and probably oxygen in the Tumbiana depositional environment, 300 million years before the oxygenation of the Earth's atmosphere.