

Peering into the Cradle of Life: multiple sulphur isotopes reveal insights into environmental conditions and early sulphur metabolism some 3.5 Ga ago

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During the early stages of Earth's evolution, environmental conditions were much different from today. The early atmosphere was reducing with abundant carbon dioxide and methane, but largely devoid of oxygen ($<10^{-5}$ PAL), while the ocean was anoxic [1]. Hence, life emerged and evolved under inhospitable environmental conditions.

A multiple sulphur isotope approach (^{32}S , ^{33}S , ^{34}S , and ^{36}S) is used for tracing life on Earth as well as characterizing the prevailing environmental conditions. As a matter of fact, the preservation of distinctly different $\Delta^{33}\text{S}$ signals into the sedimentary realm is possible only under anoxic atmospheric conditions, with a maximum level of atmospheric oxygen of 10^{-5} PAL [2].

The Barberton Greenstone Belt in South Africa (3.55-3.23 Ga) represents one of the oldest well preserved rock successions from the earliest part of Earth history. Three sets of samples from the Barberton were analyzed so far.

Barite from the Mapepe Formation is part of the 3.23-3.26 Ga old Fig Tree Group. It is characterized by a sulphur isotopic composition ($\delta^{34}\text{S}$) between 2.9 and 7.7‰ (avg. $4.0 \pm 1.0\text{‰}$; n=39) and an oxygen isotopic composition ($\delta^{18}\text{O}$) between 7.6 and 13.0‰ (avg. $10.3 \pm 1.4\text{‰}$; n=35).

Massive sulphides are from two different deposits. The Bien Venue sulphides are characterized by $\delta^{34}\text{S}$ values ranging from 0.7 to 3.5‰ while Mhlati sulphides display slightly negative $\delta^{34}\text{S}$ values between -1.2 and -0.1‰. All results are close to the 0‰ and could resemble a juvenile sulfur source. In contrast, both sets of samples show totally different $\Delta^{33}\text{S}$ values. Samples from the Mhlati deposit yielded a range from 2.657 to 3.152‰ while the Bien Venue Prospect samples vary between -0.160 and -0.130‰.

Komatiites and tholeiites are from the type locality at the Komati River. Five out of six samples are characterized by near-zero $\Delta^{33}\text{S}$ values between -0.200 and -0.090‰. $\delta^{34}\text{S}$ values for these samples range from -0.69 to 0.34‰. However, one sample displays a $\Delta^{33}\text{S}$ value of -0.507‰ which reflects mass-independent sulphur isotope fractionation, while showing a $\delta^{34}\text{S}$ value of +5.0‰.

Some preliminary conclusions can be drawn with respect to the sulphur source and the possible pathway of sulphur turnover. Barite is characterized by $\Delta^{33}\text{S}$ and $\delta^{34}\text{S}$ results that are very different from those for komatiites and massive sulphides. $\Delta^{33}\text{S}$ values in barite represent mass-independently fractionation which reflects the atmospheric signal. Komatiites and massive sulphides from the Bien Venue prospect are indeed characterized by comparable $\Delta^{33}\text{S}$ and $\delta^{34}\text{S}$ values, which suggest a common sulphur supply, specifically a juvenile source. Besides, $\Delta^{33}\text{S}$ values represent a mass-dependent fractionation. On the contrary, massive sulphides from the Mhlati deposit are significantly different in their multiple sulphur isotopic composition. These samples display a sizeable mass-independent sulphur isotope fractionation, while the Bien Venue Prospect samples represent a mass-dependent fractionation signal. Moreover, the sulphides from the Mhlati deposit show a linear negative correlation between the $\Delta^{33}\text{S}$ and $\Delta^{36}\text{S}$ values of -1.7, typical for Archean sedimentary sulphides.

References:

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- [2] Pavlov, A.A., and Kasting, J.F., 2002. Mass-independent fractionation of sulphur isotopes in Archean sediments: strong evidence for an anoxic Archean atmosphere. *Astrobiology* 2: 27-41.