

## Deconvolution of the sulfur cycle in Archean sulfate deposits using quadruple sulfur isotope ( $^{32}\text{S}$ , $^{33}\text{S}$ , $^{34}\text{S}$ , $^{36}\text{S}$ ) analyses

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The geological record of Archean sulfate consists of several barite deposits located in Western Australia, India and South Africa. These sulfate deposits formed episodically between 3.5 and 3.2 Ga ago and are associated with felsic volcanoclastic sediments. In a  $\delta^{34}\text{S}$ - $\Delta^{33}\text{S}$  diagram, the sulfate and associated sulfides define a negative trend interpreted to reflect the conjoint effect of a mass dependent fractionation process (MDF;  $\delta^{34}\text{S}$ ) overprinting a mass independent fractionation process (MIF;  $\Delta^{33}\text{S}$ ) of photolytic origin. The MIF-S correlation has been attributed to episodes of intense volcanism with important releases of  $\text{SO}_2$  into the atmosphere [1]. In order to better understand the sulfur cycle associated with the formation of the barite deposits we performed a 4-S-isotope study of the samples from Australia and South Africa previously investigated for their 3 sulfur isotopes as well as new samples from India.

Bulk and *in situ* S-isotope analyses have been performed on barite and pyrite from various sedimentary rocks. Pyrite in ultramafic rocks and deep-water carbonaceous cherts show a negative  $\Delta^{36}\text{S}$ - $\Delta^{33}\text{S}$  trend of slope -0.9, which overlaps the generally observed trend in Archean sediments attributed to a specific UV-photolysis in an anoxic atmosphere. In contrast, pyrite in barite and associated terrigenous and volcanoclastic sediments follow different  $\Delta^{36}\text{S}$ - $\Delta^{33}\text{S}$  trends consistent with different UV-photolysis processes possibly overprinted by MDF processes. Moreover, *in situ* 4-S-isotope analysis of barite shows that several populations of sulfate have been preserved. This suggests that previous bulk analyses of the barite deposits correspond to a mixing of different sources of sulfate of different origins. These results allow discussing the specific role of bacterial sulfate reduction on the formation of the Archean sulfate reservoirs and associated sulfides.

[1] Philippot *et al.* (2012) *Nature Geoscience* **5**(9), 668-674.