# Geographic and lithologic test of the Mesoarchaean S-MIF minimum

KRISTYN RODZINYAK[1*], LÉA BRASCHI[1], CHRISTIE ROWE[1], ANDREY BEKKER[2], PHILLIPS THURSTON[3], BOSWELL WING[1]

[1]McGill University, Earth and Planetary Sciences, Montreal, Canada, kristyn.rodzinyak@mail.mcgill.ca (* presenting author)

[2] University of Manitoba, Geological Sciences, Winnipeg, Canada

[3] Laurentian University, Department of Earth Sciences, Sudbury

The disappearance of mass independent fractionation in sulfur isotopes (S-MIF) around 2.45 billion years ago is associated with an increase in atmospheric oxygen content. However, the large S-MIF that characterizes the Archaean has not yet been identified in Mesoarchaean (3.2 to 2.8 Ga) rocks. This diminished variability has been attributed to atmospheric compositional changes including fluctuations in atmospheric oxygen, variations in volcanic $SO_2$- $H_2S$ ratios, and high-altitude methane hazes. In order to constrain the geographic and lithologic distribution of the diminished Mesoarchaean S-MIF signal, we obtained S isotope data from a variety of lithologies from previously uninvestigated Mesoarchaean terrains.

Samples were collected from four greenstone belts within the Superior Province in Northwestern Ontario (Finlayson Lake, Lumby Lake, Red Lake, and Woman Lake) that span an age range of 2.99 to 2.87 Ga. Metamorphic grade within the sampled portions of each belt is no higher than greenschist facies. We studied multiple lithologies, including shales, cherts, carbonates, banded iron formation (BIF), volcanic massive sulfide (VMS) showings, pillow basalts as well as greywackes and phyllites of volcanoclastic and siliciclastic origin. Whole rock samples and individual macroscopic sulfide grains were analyzed for their multiple S isotope compositions.

Sulfide $\delta^{34}S$ values range from -4.6‰ to 8.9‰ V-CDT, while the associated $\Delta^{33}S$ values range from -0.93‰ to 2.32‰ V-CDT. Samples with significant $\Delta^{33}S$ values also have $\Delta^{36}S$ values that fall on a slope of approximately -1, which is typical for Archaean S-MIF. The clastic rocks in our sample suite exhibit near-zero $\Delta^{33}S$ values, while the non-clastic rocks preserve significant S-MIF.

Macroscopic pyrites within some samples show resolvable differences in their multiple S isotope compositions. For example, the silica-rich layers in BIF seem to have more positive $\delta^{34}S$ and $\Delta^{33}S$ values compared to the silica-poor layers. Other samples contain different types of sulfides with similar isotopic compositions. Chalcopyrite and pyrite grains within a single VMS sample, for example, show negligible difference in their multiple S isotope compositions.

Compared to literature data for the Mesoarchaean, we observe a slightly larger spread in both $\delta^{34}S$ and $\Delta^{33}S$ values. The overall S-MIF range is still much reduced relative to the rest of the Archaean. The identification of diminished S-MIF range in multiple localities and lithologies (including shales, carbonates, cherts, and BIFs) suggests that this is a primary feature of the Mesoarchaean atmosphere rather than the effect of sampling bias. This interpretation is supported by the lithologic controls on S-MIF preservation that we have identified here.

Despite the reduced S-MIF magnitude, the full Mesoarchaean sulfur isotope distribution shows similar systematics to other parts of the Archaean. For example, the observed $\Delta^{33}S$ and $\delta^{34}S$ variability can be explained by covariation along the Archean reference array and a horizontal spread of $\delta^{34}S$ values all with similar -$\Delta^{33}S$ values. These features suggest that the diminished Mesoarchaen S-MIF record may be best explained through dilution by a S source without S-MIF, either in the atmosphere or in the marine reservoir, rather than by changing the photochemical regime producing S-MIF.

# Searching for traces of early life in Earth's oldest sulfate deposit: the ca. 3520 Ma Londozi barite, Swaziland

DESIREE ROERDINK[1*], PAUL MASON[1], FRAUKJE BROUWER[2], MARTIN WHITEHOUSE[3], NOAH NHLEKO[4]

[1]Department of Earth Sciences, Utrecht University, Utrecht, The Netherlands, d.l.roerdink@uu.nl (*presenting author), p.mason@uu.nl

[2]Department of Petrology, VU University, Amsterdam, The Netherlands, fraukje.brouwer@vu.nl

[3]Swedish Museum of Natural History, Stockholm, Sweden, martin.whitehouse@nrm.se

[4]Geological Survey and Mines Department, Mbabane, Swaziland, nhlekon@swazi.net

Microbial sulfate reduction may have been one of the earliest metabolisms to emerge on Earth. Paleoarchean pyrite and barite deposits potentially record such metabolic activity through stable sulfur isotope fractionation, but this requires proof that microbial signatures were not obscured by metamorphic processes. Here, we discuss the origin of isotopically depleted pyrite in the oldest known sulfate deposit on Earth: the Londozi barite in western Swaziland, for which we obtained a minimum age of 3521±13 Ma by U-Pb zircon dating of felsic volcanics overlying the barite.

Field evidence indicates that the barite was formed in a low-energy marine environment with dominant mafic volcanism and intense hydrothermal activity. It was subsequently affected by amphibolite facies metamorphism and extensive metasomatism. Dominant mineral assemblages include Ca-rich phases actinolite, diopside and epidote with secondary Ba-rich feldspar (celsian and hyalophane) and witherite.

SIMS multiple sulfur isotope analyses of pyrite in the Londozi deposit identified three distinct populations of sulfide: (1) barite-hosted grains with average $\delta^{34}S$ = -5.2‰ and $\Delta^{33}S$ = -1.0‰ (n = 18), (2) massive chert-hosted grains with average $\delta^{34}S$ = -1.1‰ and $\Delta^{33}S$ = 0.2‰ (n = 7) and (3) grains in a silicified silicate matrix with average $\delta^{34}S$ = -0.2‰ and $\Delta^{33}S$ = -0.6‰ (n = 71). We hypothesize that silicate-hosted pyrite was derived from a sulfide pool generated by microbial reduction of sulfate, showing a shift in $\delta^{34}S$ of 5-8‰ relative to the barite. In contrast, association of the most $^{34}S$-depleted pyrite with barite might not reflect microbial processes, but could represent sulfide produced during metasomatic remobilization of the barite by reductive dissolution. This process is in agreement with an average sulfur isotope temperature of 524°C calculated for barite-pyrite mineral pairs, and explains the presence of secondary barium-rich feldspar with increasing Ba content towards the barite.

Our work, therefore, demonstrates that the geological context of isotopically depleted sulfides must be carefully interpreted before arguing for the presence of sulfate reducing prokaryotes in the Paleoarchean.