Goldschmidt 2025 Abstract
https://doi.org/10.7185/gold2025.30198

Triple oxygen isotope evidence for thermophilic microbial sulfate reduction in the Paleoarchean

DR. DESIREE L. ROERDINK[1] AND ILYA N. BINDEMAN[2]

[1]Department of Earth Science, University of Bergen
[2]University of Oregon

Paleoarchean (3.6-3.2 Ga) bedded barite deposits from the Kaapvaal, Pilbara and Dharwar cratons have provided important insights into the earliest sulfur cycle [1]. However, the role of microbial sulfate reduction in the early environment remains debated due to ambiguities in the interpretation of barite sulfur isotope data [2,3]. Here, we present the triple oxygen isotopic compositions of all major Paleoarchean barite occurrences to reassess roles of atmospheric versus microbial processes during barite formation. We find both positive and negative oxygen isotope anomalies ($\Delta^{17}O$), suggesting that oxygen isotopic compositions were modified after the generation of sulfate by atmospheric SO_2 photolysis in an anoxic, ozone-free atmosphere. Within individual deposits, $\Delta^{17}O$ values are negatively correlated with $\delta^{18}O$, and shifted away from estimated photolytic sulfate composition ($\Delta^{17}O$ ~ 1‰) towards oxygen isotopic equilibrium with ice-free seawater and/or seawater-derived hydrothermal fluids. This observed shift is best explained by (partial) re-equilibration of sulfate oxygen with H_2O during microbial sulfate reduction, as abiotic equilibration reactions are too slow (100s-1000s of years) under the low-temperature (<200°C) conditions of barite formation inferred from field and geochemical data. Similarly, abiotic sulfide oxidation by Fe(III) does not produce the oxygen isotope effects observed in the barite data. Instead, sulfite produced by the reduction of adenosine phosphosulfate (APS) in the cells of sulfate reducers can rapidly exchange oxygen isotopes with intracellular water, and the reversibility of this enzymatic step produces extracellular sulfate in apparent oxygen isotope equilibrium with ambient water [4]. Based on our observed $\Delta^{17}O$-$\delta^{18}O$ trends we infer that this isotopic exchange occurred at temperatures of 50-100°C, suggesting the presence of thermophilic sulfate-reducing micro-organisms in Paleoarchean barite-forming environments.

[1] Farquhar et al (2000) Science, 289, 756-758; [2] Philippot et al (2012) Nat Geosci, 5, 668-674; [3] Roerdink et al (2012) EPSL, 331-332, 177-186; [4] Cao and Bao (2021) RiMG, 86, 463-488.