

Oxidative sulfur cycling and microbial colonization of the continents 3.2 Ga ago

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Sulfate minerals are rare in the Archean rock record and largely restricted to barite (BaSO₄) with controversially debated origin. However, the mass-independent fractionation of sulfur isotopes in these and other Archean sedimentary rocks shows that photolysis of volcanic aerosols in an oxygen-poor atmosphere played an important role in their formation. Here, we report on the multiple sulfur-isotopic composition of the to-date oldest sedimentary anhydrite of the geological record in the ca. 3.22 Ga Moodies Group of the Barberton Greenstone Belt, South Africa. There, anhydrite occurs, together with barite and pyrite, in regionally traceable paleosols that formed in fluvial settings. Variable abundance of barite vs. anhydrite possibly reflects changes in sulfate enrichment by evaporitic concentration across orders of magnitude in an arid, nearshore terrestrial environment, periodically replenished by new influx of sea water. Multiple S-isotope composition of anhydrite and pyrite is consistent with microbial sulfate reduction. Juvenile S-isotope signatures in barite suggest an additional, possibly oxidative sulfate source possibly derived from continental weathering of pyrite. Although depositional environments of Moodies sulfates differ strongly from the marine barite deposits their sulfur-isotopic composition indicates that both display a primary isotopic signature. The data indicate that a constant input of small portions of oxidized sulfur phases from the continents into the Paleoproterozoic ocean may have contributed to the observed long-term increase of $\Delta^{33}\text{S}_{\text{sulfate}}$ values.