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Sulfate in the Paleoproterozoic Oceans: insight from barite deposits and their surrounding sedimentary rocks in the Barberton Greenstone Belt

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The sulfur isotope record indicates depleted sulfate levels in the Archean oceans, reflecting limited input of oxidized sulfur species as the end-products of atmospheric photolysis under widespread anoxic conditions [1,2]. In contrast, barite deposits occur in the Palaeoproterozoic (3.5-3.2 Ga) across several different greenstone belts, and have been interpreted to represent spatial or temporal increases in marine sulfate concentrations. Until recently, the origin and extent of these enrichments was based largely on sulfate mineral abundances. Multiple sulfur isotope data for pyrite and barite provide a new and more powerful insight for assessing sulfate levels as our knowledge of the Archean sulfur cycle has improved [3].

In this study we compile multiple sulfur isotope data in pyrite and barite from across the Barberton Greenstone Belt, Kaapvaal Craton in order to further investigate the extent and origin of sulfate enrichments. We use bulk rock geochemistry, as well as element mapping and iron isotope data in pyrite to further constrain the origin of complex populations of sulfide minerals. Samples were obtained from drill core and mine sections, with a focus on material from the recently-completed Barberton Greenstone Belt drilling project. Pyrite and barite were measured in samples from the 3.52 Ga Theespruit formation (Londozi Mine), the 3.4 Ga Buck reef chert (BARB3 drill core), 3.26 Ga Bien Venue formation (Stentor and Amo mines) and the 3.26-3.23 Ga Lower Mapepe Formation (BARB3, BARB5 and ETC1975 drill cores). We present both new and previously published data [4-6]

Pyrite $\delta^{56}\text{Fe}$, coupled with mineral mapping of the trace elements Ni, As, Cu, Se and Co, proved effective for the delineation of pyrite populations and pathways of pyrite formation. Pyrites were split into petrographic and geochemical groupings which enabled more accurate identification of sulfur species of atmospheric origin. The most primary sulfur isotope data support conventional models of atmospheric photolysis where a positive $\Delta^{33}\text{S}$ was derived from heterogeneous photolytic elemental S, with negative $\Delta^{33}\text{S}$ capturing a homogenized marine sulfate reservoir.

Pyrite multiple S isotope data closely track the abundance of barite in the surrounding host rocks, suggesting that marine sulfate levels were generally low and that sulfate increases were sporadic and localized. Multiple S isotopes in barite suggest the widespread operation of microbial sulfate reduction throughout the Paleoproterozoic. We speculate that biological evolution was responsible for the Paleoproterozoic marine enrichment and Neoproterozoic relative depletions in sulfate abundance.

References:

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