

Sr isotopic insights into the formation of Paleoproterozoic barite

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Paleoproterozoic barites are important targets for studying the earliest environments and emergence of microbial metabolisms on Earth. However, the origin and formation of these rare stratiform sulfate deposits remains poorly understood. Sulfur isotope data suggest that sulfate was derived from seawater [1], but the source of Ba and geological setting in which the barites precipitated are less well constrained.

Here, we present Sr isotope data from four Paleoproterozoic barite deposits from the Barberton Greenstone Belt in South Africa and Swaziland, with ages ranging from 3.52 Ga (Londozi) to *ca.* 3.4 Ga (Vergelegen), 3.26 Ga (Stentor) and 3.23-3.26 Ga (Barite Valley). Barite has extremely low ⁸⁷Rb/⁸⁶Sr due to crystallographic exclusion of Rb and therefore very limited *in situ* radiogenic growth of ⁸⁷Sr, so that measured ⁸⁷Sr/⁸⁶Sr ratios reflect the source of Sr during initial barite precipitation. We demonstrate that all barite deposits show a relative large range in ⁸⁷Sr/⁸⁶Sr that appears to be of primary origin and not related to metamorphic grade. The lowest ⁸⁷Sr/⁸⁶Sr-values for individual deposits define a strong correlation with age ($R^2 = 0.98$) and increase from 3.5 to 3.2 Ga following a slope that is significantly steeper than the upper mantle curve. These results suggest the presence of a temporally homogeneous reservoir with higher Rb/Sr-values than the Paleoproterozoic mantle, and argues against a simple genetic model with mixing of mantle-derived Ba with seawater SO₄²⁻. The highest ⁸⁷Sr/⁸⁶Sr-values exceed ratios inferred for Paleoproterozoic seawater but are close to values suggested for continental crust at 3.5 Ga [2]. In addition, Sr-isotope ratios are correlated with atmospherically-derived sulfur isotopic variations, showing decreasing magnitudes of $\Delta^{33}\text{S}$ with increasing ⁸⁷Sr/⁸⁶Sr and possibly demonstrating coupling of surface and deep processes during the formation of Paleoproterozoic barite.

[1] Roerdink et al (2012) *Earth Planet. Sci. Lett.* **331-332** (177-186) [2] McCulloch (1994) *Earth Planet. Sci. Lett.* **126** (1-13)