

Multiple ($^{32}\text{S}/^{33}\text{S}/^{34}\text{S}/^{36}\text{S}$) sulfur isotope analysis of early Archean barite and pyrite: new insights into ancient sulfate reduction

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One of the oldest barium sulfate (barite) deposits occur in the ~3.5 billion-years-old (Ga) Dresser Formation, Western Australia. This barite has been considered by many investigators to be evaporitic sediment that were silicified by later fluid circulation (e.g., Lowe 1983; Buick and Dunlop, 1990). Also, the barite contains ^{34}S -depleted pyrites, suggesting metabolic activity of sulfate-reducing microbes in shallow marine setting (Shen et al., 2001). If correct, the barite-associated pyrite is the oldest evidence for microbial sulfate reduction. On the contrary, second and third alternative models for the Dresser barite-pyrite associations have been proposed previously. The second model is that the pyrites would have been deposited directly from hydrothermal H_2S , which was partly oxidized by non-oxygenic phototrophs into sulfate and subsequently deposited as barite (Lambert et al., 1978). The third model is that SO_2 -rich magmatic fluid would have disproportionated to form H_2S and SO_4^{2-} and precipitated pyrites and barite without any microbial interaction (Runnegar, 2001; Van Kranendonk and Pirajno, 2004). In order to test these models, we newly measured multiple sulfur isotope ratios ($^{32}\text{S}/^{33}\text{S}/^{34}\text{S}/^{36}\text{S}$) for the barite and pyrite as well as related igneous rocks, and propose a fourth model. The barite and pyrite therein all show negative D^{33}S and positive D^{36}S non-mass-dependent signature, whereas the sulfides in related igneous rocks are mass-dependent. The results indicate that the barite would have been derived from seawater sulfate, but not from magmatic sulfur. Also, the pyrite shows 15–22 permil d^{34}S -depletion relative to co-existing barite with similar but not identical D^{33}S values. These isotopic relationships can be explained either by thermochemical sulfate reduction at 250 to 350°C or by microbial sulfate-reduction from seawater sulfate, but not from magmatic sulfur. The two alternatives may be potentially distinguished from their characteristic $\text{D}^{33}\text{S}/\text{D}^{36}\text{S}$ relationships observed in this study.