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

Yuichiro Ueno[1]; Shuhei Ono[2]; Douglas Ramble[2]


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 34S-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 H2S, which was partly oxidized by non-oxygenic phototrophs into sulfate and subsequently deposited as barite (Lambert et al., 1978). The third model is that SO2-rich magmatic fluid would have disproportionated to form H2S and SO42- 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 (32S/33S/34S/36S) for the barite and pyrite as well as related igneous rocks, and propose a fourth model. The barite and pyrite therein all show negative D33S and positive D36S 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 d34S-depletion relative to co-existing barite with similar but not identical D33S 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 D33S/D36S relationships observed in this study.