Quadruple sulfur isotope constraints on the origin of the early Archean barite and pyrite

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One of the oldest barium sulfate (barite) deposits occur in the ~3.5 billion-years-old Dresser Formation, Western Australia. The barite contains ^{34}S-depleted pyrite, suggesting metabolic activity of sulfate-reducing microbes in shallow marine setting, thus representing the oldest evidence for microbial sulfate reduction [1]. Recent field observations of the barite, however, suggest that the barite-pyrite would have been precipitated from hydrothermal fluid [2,3].

We measured multiple-sulfur isotope ratios ($^{32}S/^{33}S/^{34}S/^{36}S$) for the barite and pyrite as well as related igneous rocks by newly developed analytical protocol [4]. The barite and pyrite therein all show negative $\Delta^{33}S$ and positive $\Delta^{36}S$ non-mass-dependent signature, whereas the sulfides in the related igneous rocks are mass-dependent, suggesting that sulfur in barite and pyrite is derived from seawater sulfate, not from disproportionation of magmatic SO_2 [3]. Vein and bedded barites show indistinguishable and uniform $\delta^{34}S$ values (+4.7±0.7‰; n=9), supporting seawater origin of the Dresser barite, and suggesting that sulfur source would be the same for vein and bedded barites. Also, the barite-pyrite pair shows 15~22‰ $\delta^{34}S$-fractionation on a secondary mass dependent line of slope ($\delta^{33}S/\delta^{34}S$) less than 0.512, which are slightly different from that of equilibrium mass dependent fractionation (0.515). Moreover, $\Delta^{33}S/\Delta^{36}S$ ratio of the barite-pyrite pair deviated from empirical Archean mixing line ($\Delta^{36}S/\Delta^{33}S = -1$). These characteristic isotope ratios of the barite-pyrite pairs are consistent with mass dependent fractionation [4], and imply that the pyrite would have been produced by microbial or thermochemical reduction of seawater sulfate. Resolution of microbial-vs-thermochemical sulfate reductions must await additional experimental work, though the observed slope of less than 0.512 for the barite-pyrite pair is consistent with kinetic microbial process, but not with thermodynamic equilibrium.

References

[1] Shen Y., Buick, R., and Canfield, D. *Nature* **410,** 77-81.

[2] Runnegar, B. 2001, *Goldschmidt2001 abst.*, 3859.

[3] Van Kranendonk, M.J. and Pirajno, F. *Geochem. Exprol. Env. Anal.* **4,** 253-278.

[4] Ono S., Wing, B., Johnston, D., Farquhar, J. and Rumble, D., *Geochem. Cosmochim. Acta*. **70,** 2238-2252.