Multiple sulfur isotopes (32S, 33S, 34S, and 36S) of the Archean deposits: Biogeochemical sulfur cycle under O2-poor atmosphere

Yuichiro Ueno[1]; Douglas Ramble[2]; Shuhei Ono[2]; Shigenori Maruyama[3]

[1] Earth Science and Astronomy, Univ. Tokyo; [2] Geophysical Lab.; [3] Earth and Planetary Sci., Tokyo Institute of Technology

Recent discovery of mass-independent sulfur isotope fractionations in pre-2.3 Ga sedimentary rocks provided new insights into the Earth's early sulfur cycle (Farquhar et al., 2000). It has been hypothesized that photo-dissociation of SO2 gas in the O2-poor early atmosphere produced the mass-independent fractionation in 33S, thereby yielding a negative D33S value (~ d33S - 0.515 x d34S) of the Archean seawater sulfate and positive D33S of more reducing sulfur species (Farquhar et al., 2001; Ono et al., 2003). Therefore, multiple sulfur isotope analyses (32S, 33S, 34S, and 36S) of Archean sulfide and sulfate have potential to determine the source of sulfur and provide better understand of biogeochemical sulfur cycle under the O2-poor Archean atmosphere. We performed multiple sulfur isotope analyses (32S, 33S, 34S, and 36S) by a new laser fluorination microprobe, using an excimer laser for in situ spot analyses of sulfide minerals, and by chemical extraction-fluorination for disseminated pyrite and sulfate minerals by the procedure developed by Hu et al. (2003) and Ono et al. (2003). Analyzed samples are from wide range of Archean to Early Proterozoic rocks including sedimentary rocks, igneous rocks, and hydrothermal veinlets. The result reconfirmed that some pre-2.3 Ga sulfides and sulfates show non-zero D33S anomaly. We identifed negative correlation between D33S and D36S (~ d36S - 1.91 x d34S), which is consistent with experimental results of photo-dissociation of SO2 (and/or SO) (Farquhar et al., 2001). This strongly supports the hypothesis that the negative D33S is derived from sulfate aerosol and positive from elemental sulfur, both of which was produced by SO2 (or SO) photolysis. We also identified that the sulfides in a single hand specimen generally show homogeneous D33S with small d34S variation (~2 permil). Thus, d34 vs D33S diagram is useful to deduce the biogeochemical sulfur cycle under O2-poor early atmosphere. The observed variation of d34S and D33S of sulfides indicate that both sulfate reduction and elemental sulfur reduction would have been important for the sulfur cycle at that time.

References: Farquhar et al. 2000, Science 289, 756-758; Farquhar et al. 2001, JGR 106, 32829-32840; Hu et al., 2003, GCA 67, 3101-3117; Ono et al., 2003, EPSL 213, 15-30; Ueno et al., 2004, GCA 68, 573-589