

Mass-independent isotopic fractionations of sulfur recorded in sulfides from Paleoproterozoic Huronian Supergroup

Naoki Yamada[1]; Shogo Tachibana[2]; Yuichiro Ueno[3]; Subaru Tsuruoka[4]; Mayuko Nakagawa[5]; Naohiro Yoshida[6]; Eiichi Tajika[7]

[1] Earth and Planet. Env. Sci, Univ. Tokyo; [2] Earth and Planet. Sci., Univ. of Tokyo; [3] Global Edge Inst., Tokyo Tech.; [4] Earth and Planetary Sci., Tokyo Institute of Technology; [5] Applied chemistry, TITech; [6] IGSSE, Tokyo Institute of Technology; [7] Dept. Earth Planet. Sci., Univ. of Tokyo

Mass-independent isotopic fractionation (MIF) of sulfur found in sedimentary rocks older than 2470 Ma implies that the atmospheric oxygen level was lower than 10^{-5} PAL (present atmospheric level) in the Archean atmosphere if the MIF was caused by photochemical reactions of volcanic SO₂. Sulfides from the Rooihogte and Timeball Hill Formations, Transvaal Supergroup, South Africa, (2316 +/- 7 Ma; Hannah J. L. et al., 2004, EPSL) show only a small degree of MIF [Bekker A. et al., 2004, Nature], suggesting that the atmospheric oxygen level reached 0.00001 PAL by 2316 Ma. The Huronian Supergroup in E. Canada records three Paleoproterozoic glacial events between ~2450 and ~2220 Ma, and may record the evidence of the great oxygenation event. The sulfur isotopic compositions of sulfides in the Matinenda to Gordon Lake Formations of Huronian Supergroup exhibit D³³S, deviation from a mass-dependent fractionation line, of less than 0.5 permil [e.g., Farquhar J. et al., 2000, Science]. Ion microprobe analyses showed that sulfides from the McKim and Pecors Formations preserve D³³S of 0.7-0.9 permil, which may represent the last remnants of a reducing atmosphere [Papineau et al., 2007, GCA]. However, there are sparse data on multiple sulfur isotopes from Paleoproterozoic samples. In this study, in order to increase data sets on Paleoproterozoic multiple sulfur isotopes and to put some constraints on diminishing and disappearing of sulfur MIF signatures, we performed multiple sulfur isotopic analyses of sulfides from Huronian Supergroup.

Sulfur was extracted from powdered core samples (KERR- McGEE 150-4) of Huronian Supergroup via chromium reduction, and was converted to Ag₂S and finally to SF₆. Sulfur isotopic analyses (³²S, ³³S, ³⁴S, and ³⁶S) were carried out for purified SF₆ using a Thermo-Finnigan MAT 252 mass spectrometer at Tokyo Institute of Technology.

Clear evidence of sulfur MIF was found from pyrite and pyrrhotite in the Serpent Formation (D³³S of ~+1.2 permil and D³⁶S of -1.5~-2 permil), and sulfides in the McKim Formation may also have signatures of sulfur MIF (D³³S of ~+0.5 permil and D³⁶S of -0.3~-1.2 permil). The magnitude of MIF observed in the Serpent Formation is the largest among those reported from Huronian Supergroup. The Serpent Formation overlies the McKim and Pecors Formations, where D³³S of ~0.7-0.9 permil were reported [Papineau et al., 2007], and may be younger than the Rooihogte and Timeball Hill Formations in Transvaal Supergroup with little or no sulfur MIF [Bekker et al., 2004]. This implies that the onset of the Great Oxygenation event may have been younger than 2316 Ma. However, mineral assemblages and textures of sulfides in the Serpent Formation may suggest that they experienced hydrothermal events, and the source of sulfur with MIF for the Serpent Formation should be clarified in future studies.