Implications of the Absence of Mass Independent Sulfur Isotope Fractionation in 2.76 Ga Lacustrine and 3.0 Ga Marine Sediments

Yumiko Watanabe[1]; Hiroaki Ikemi[2]; Hiroshi Ohmoto[3]

[1] Astrobiol. Res. Center and Dept. of Geosc., Penn State Univ.; [2] Insit. of Env. Sys., Kyushu Univ.; [3] PSARC,Penn State

The presence of mass independent fractionation (MIF) of S isotopes in pre-2.0 Ga rocks and the absence of MIF in younger rocks have been regarded by many recent investigators as the best evidence for a dramatic change in the atmospheric oxygen level, from anoxic to oxic, at 2.35 Ga. This is because the MIF of S has been linked to the photochemical reactions of volcanic SO2 in the absence of an ozone shield to produce S0 with large positive D33S values (more than 50 permil) and SO42- with negative D33S values (less than -10 permil).

The mineralogy and geochemistry, including multi-sulfur isotopes, are investigated on drill core samples from two Archean shale formations, recovered from the Pilbara district, Australia by the Archean Biosphere Project. One core intersected a more than 150 m-thick sand-stone/shale unit (the Hardey Formation), which is the oldest (2.76 Ga) lacustrine formation. The other core intersected a more than 180m-thick shale unit (the Mosquito Creek Formation), which is a major marine formation of 3.0 Ga in age. Twenty-six samples were collected with a 2.5-m interval from a intercalated argillite unit (55m thick) of the Hardey Formation, and 27 samples are collected with a few meters interval from three intercalated argillite units (several meters think) of the Mosquito Creek Formation. These formations were subjected to zeolite- or lower greenschist-facies metamorphism, but are considered the least altered Archean samples. Bedding planes are well preserved in most studied samples, and no obvious deformation/alteration signature is recognizable.

Essentially all the sulfur in the studied samples occurs as pyrite. The lucustrine Hardey shales have uniformly low contents of sulfide S (0.01 to 0.08 wt%) and low S/Corg ratios (less than 0.1). In contrast, the marine Mosquito shales have higher contents of S (0.01 to 1.00 wt%) and higher S/Corg ratios (more than 0.3). These data are not compatible with a currently popular idea of low-sulfate Archean oceans (e.g., Canfield et al., 2000). The occurrence, morphology and content of pyrite grains as well as their host rock mineralogy and chemistry suggest that the pyrite crystals in these shales were not detrital grains of igneous rocks, but formed within the host sediments during early diagenetic stage (i.e., diagenetic pyrite) and/or in the overlying water bodies (i.e., syngenetic pyrite) by sulfate-reducing bacteria.

The d34S values vary approximately 5 permil among 20 samples from each formation, but their D33S values fall within a range of +-0.3 permil there is no evidence of MIF in these formations. Possible interpretations of our results include, but not restricted to, the following: (1) the Archean atmosphere fluctuated between oxic and anoxic if atmospheric photochemical reactions are only cause for MIF; (2) the large MIF values observed in some pre-2.0 Ga sedimentary rocks were produced by atmospheric reactions when explosive volcanisms emitted large amounts of SO2 to the stratosphere; and (3) large MIF values in some geologic samples were caused by mechanisms other than atmospheric photochemical reactions. (2) and (3) imply that the presence or absence of MIF in geologic samples is not a measure of atmospheric pO2 level. (3) is a reasonable explanation because of: (a) the recognition of strong correlations between the MIF-S values and the degree of hydrothermal alteration in samples from the 2.55 McRae Shale and the 2.76 Jerrinah Formation that were previously analyzed by Ono et al. (2003); and (b) the recent findings by nuclear chemists (e.g., Fujii, et al., 2002) of MIF of many elements during non-photochemical reactions.