

## Linking multiple sulfur isotopic characteristics of Archean sedimentary rocks to their depositional environments

WATANABE, Yumiko<sup>1\*</sup>, HAMASAKI, Hiroshi<sup>1</sup>, CHORNEY, Andrew<sup>1</sup>, OHMOTO, Hiroshi<sup>1</sup>

<sup>1</sup>Penn State University

Many researchers have linked the anomalously fractionated (or commonly called mass independently fractionated) isotopes of sulfur (AIF-S or MIF-S) in sedimentary rocks to UV photolysis of volcanic SO<sub>2</sub> and to an O<sub>2</sub>-poor atmosphere. However, serious discrepancies exist between the AIF-S signatures in natural samples and those of the products (S<sub>0</sub> and SO<sub>4</sub><sup>2-</sup>) of SO<sub>2</sub> photolysis using a broad-band UV lamp which simulates the sun light. The produced S<sub>0</sub> and residual SO<sub>2</sub> possess only very small AIF-S signatures (i.e.,  $\delta^{33}\text{S}/\delta^{34}\text{S} = 0.58 \pm 0.04$ ). Based on theoretical and experimental investigations, we have proposed that the AIF-S signatures in some (if not all) Archean sedimentary rocks were produced by chemisorption-redox reactions involving solid phases (e.g., organic matter, iron oxides, carbonates, clays and aqueous S-bearing species (SO<sub>4</sub><sup>2-</sup> and H<sub>2</sub>S) during the diagenesis of sediments in hydrothermal environments. According to our model, the characteristics of AIF-S signatures may vary depending conditions of the chemisorption-redox reactions (e.g., type and surface area of the solid phase, concentration of the aqueous species, temperature, reaction time, open or closed-system). To evaluate the validity of our model, we have examined the relationships among the AIF-S characteristics ( $\delta^{34}\text{S}$ ,  $\Delta^{33}\text{S}$  and  $\Delta^{36}\text{S}$  values) of sulfides and sulfates, their modes of occurrence (e.g., disseminated, nodules, layers, veins), and the lithology of their host rocks.

We have recognized that sulfides (and sulfates) that formed in similar depositional environments generally exhibit similar AIF-S characteristics. For example, sediments accumulated in closed euxinic basins under the influence of submarine hydrothermal activity (e.g., pyritic black shales and siderite-rich sediments in the 2.5 Ga McRae and 2.7 Ga Jeerinah Formations) generally possess  $+\delta^{34}\text{S}$  and  $+\Delta^{33}\text{S}$  values or  $-\delta^{34}\text{S}$  and  $-\Delta^{33}\text{S}$  values. Barite- and sulfide-bearing sediments accumulated in shallow, evaporitic basins (e.g., the 3.5 Ga Dresser and 2.7 Ga Tambiana Formations) often possess  $-\delta^{34}\text{S}$  and  $+\Delta^{33}\text{S}$  values for the sulfides and  $+\delta^{34}\text{S}$  and  $-\Delta^{33}\text{S}$  values for the barite.

The observed relationships between AIF-S signatures and depositional environments, and the frequent occurrence of sediments with no AIF-S signatures in Archean sedimentary rocks (e.g., 2.7 Ga Hardy lacustrine Formation), are difficult to explain by the current popular model that links AIF-S to atmospheric UV reactions. Rather, the data can be best explained by our model that links AIF-S to chemisorption-redox reactions (e.g., thermochemical sulfate reduction (TSR), replacement of iron oxides by pyrite) under large-scale hydrothermal conditions. Therefore, the AIF-S record of sedimentary rocks may be linked to the thermal and biological evolution of the Earth, rather than to the atmospheric evolution.

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