

## Unraveling the mystery of MIF-S in Archean sedimentary rocks

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Nearly all geoscientists have accepted the theory that the record of mass-independent fractionation of sulfur isotopes (MIF-S), defined as the ( $^{33}\text{DS} = \delta^{33}\text{S} - 0.514 \delta^{33}\text{S}$ ) values outside of  $0 \pm 0.2\%$ , in sedimentary rocks accurately reflects the evolutionary history of  $\text{O}_2$  in the atmosphere. Thus, the disappearance of strong MIF-S signatures in sedimentary rocks younger than  $\sim 2.4$  Ga in age has been believed to be indisputable evidence for the "dramatic change" from an anoxic to oxic atmosphere, which is referred to as the "Great Oxidation Event". This theory has developed because the MIF-S was supposedly created by the UV photolysis of volcanic  $\text{SO}_2$  in and  $\text{O}_2$ -poor atmosphere:  $3\text{SO}_2 + 2\text{H}_2\text{O} + \text{UV} = \text{S}^0 + 2\text{H}_2\text{SO}_4$  (R1). The  $\text{S}^0$  formed by R1 formed pyrite via reaction with  $\text{Fe}^{2+}$ -rich ocean water:  $2\text{S}^0 + \text{Fe}^{2+} + \text{H}_2 = \text{FeS}_2 + 2\text{H}^+$  (R2). However, serious problems exist with these scenarios: (a). MIF-S signatures from the atmosphere should be strongest in sediments deposited in  $\Sigma\text{S}$ -poor water bodies (e.g., lakes), but it is not the case; (b). MIF-S signatures are found primarily in organic-C-rich sedimentary rocks (i.e., black shales), which were affected by hydrothermal alteration; (c). Positive correlations exist between the sulfide and organic-C contents of the MIF-S-bearing sedimentary rocks; and (d). The behaviors of redox-sensitive elements (e.g., Fe, U, Mo, Cr, Ce) in paleosols, carbonates, cherts, and iron formations of Archean ages are essentially the same as those of the Phanerozoic ones.

Based on theoretical and experimental investigations of multiple S isotope fractionations involving surface reactions, we have proposed that the MIF-S in sedimentary rocks was created by thermochemical sulfate reduction involving organic matter (OM) (e.g., Watanabe et al., 2009). However, questions have remained as to why MIF-S is rare in younger rocks and why some OM produce MIF-S, but others do not. We have realized that the generation of reactive OM is the key to these questions. At the JpGU 2017 meeting, we reported the discovery of two types of OM in the 3.45 Ga-old Marble Bar Chert from Western Australia. One is biogenic OM, the remnant of aerobic chemolithotrophic benthic Fe-oxidizing bacteria; and the other is abiogenic OM, produced by hydrothermal-seawater reactions. Both types of OM-syntheses were carried out through the reaction  $\text{CO}_2 + 6\text{Fe}^{2+} + 0.5\text{O}_2 = \text{CH}_2\text{O} + 3\text{Fe}_2\text{O}_3 + 12\text{H}^+$  (R3), where  $\text{Fe}^{2+}$  was supplied by hydrothermal fluids, and  $\text{CO}_2$  and  $\text{O}_2$  by the local deep ocean water. The biogenic OM is large ( $\sim 1\text{-}10 \mu\text{m}$  in size), protected by cell walls, and has maintained its bacterial morphology. In contrast, the abiogenic OM occurs typically as a  $\sim 10\text{-}20$  nm-sized cluster of angstrom-sized OM particles. Such OM, compared to the biogenic OM, would be much more reactive and would therefore be preferentially utilized in thermochemical sulfate reduction to generate MIF-S. Before  $\sim 2.4$  Ga, abiogenic OM production would have been much more important than today, because: (i). The Earth's interior was hotter than today, and igneous and hydrothermal activities were more extensive in the oceans, which provided larger amounts of  $\text{Fe}^{2+}$  into the oceans; and (ii). The atmosphere were richer in  $\text{CO}_2$  ( $p\text{CO}_2 > 100$  PAL) and already  $\text{O}_2$ -rich ( $p\text{O}_2 > \sim 1$  PAL).

Compared to the biogenic OM, abiogenic OM would have decomposed to generate the substrates (e.g.,  $\text{H}_2$ , lactic acids) for heterotrophs (e.g., sulfate-reducing bacteria) at much faster rates. The kinetic S isotopic fractionation during bacterial sulfate reduction ( $^{34}\text{DS} = \delta^{34}\text{S}_{\text{SO}_4} - \delta^{34}\text{S}_{\text{H}_2\text{S}}$ ) decreases with increased rates of reduction. Consequently, the smaller  $^{34}\text{DS}$  values for pyrites in Archean sedimentary rocks, compared to those in the younger rocks, can also be explained by the higher abundance of abiogenic OM in the

Archean oceans. Therefore, the MIF-S ( $^{33}\text{S}$ ) and  $^{34}\text{S}$  records of sedimentary rocks indicate the thermal- and tectonic histories of the Earth, rather than the atmospheric  $\text{O}_2$  history.

Keywords: Mass independent fractionation of S isotopes, hydrothermal synthesis of organic matter, thermochemical sulfate reduction, bacterial sulfate reduction, Fe-oxidizing bacteria