Comment on “Iron Isotope Constraints on the Archean and Paleoproterozoic Ocean Redox State”

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Rouxel et al. (Reports, 18 February 2005, p. 1088) argued that changes in the iron isotopic composition of sedimentary iron formations (Fe oxides) of Fe sulfides (diagenetic pyrites) in black shales and showed that the values fall in distinct ranges depending on the geologic age of the shale: mostly negative (~3.5 to 0.5 per mil) before ~2.3 billion years ago (Ga); mostly positive (~0.5 to +1.0‰) between ~2.3 and 1.7 Ga; and near zero (~0.5 to +0.2‰) after ~1.5 Ga. Based on these stages and simple models for isotopic fractionation during Fe mineralization, they concluded that: (i) Diagenetic pyrites older than ~1.7 Ga used the dissolved Fe2+ in ocean water, whereas younger pyrites used the Fe from Fe silicates and Fe oxides buried in the sediments. (ii) The Fe ores were Fe2+-rich and anoxic, and the atmosphere was anoxic before ~2.3 Ga. (iii) The oceans were stratified (Fe2+-poor, oxygenated shallow water and Fe2+-rich, anoxic deep water), but the atmosphere wasoxic during ~2.3 to 1.7 Ga. (iv) Both the oceans and the atmosphere have been fully oxygenated since ~1.5 Ga. We point to several problems in Rouxel et al.’s interpretations linking the Fe isotope data to the redox history of the oceans and atmosphere.

First, Rouxel et al. (1) suggested that the δ56Fe values of Fe2+ that formed diagenetic pyrites became negative (~3.5 to ~0‰) as a result of the precipitation of very large amounts (~50% to >90%) of Fe2+ as 56Fe-enriched Fe oxides (hematite and magnetite) in banded iron formations (BIFs). They noted that ~50% precipitation of Fe oxides is similar to the estimates of Fe sink in BIFs based on phosphorus adsorption (2). However, more than 90% removal of Fe (1) is far beyond this estimate and is therefore unrealistic.

The second shortcoming of the Rouxel et al. model concerns the age relationships between the black shales and Fe oxides. The analyzed black shales (from the Jeerinah, Mt. McRae, and Gambohaan Formations) deposited in basins before, after, or at the depositions of large BIFs (i.e., the Marra Mamba, Brockman, and Kuruman IFs, respectively) (3, 4). Therefore, BIF deposition cannot be the reason for negative and variable δ56Fe values for pyrites in the older black shales.

Third, Kakegawa et al. (5) reported various features of extensive dissolution/reprecipitation of pyrites during diagenesis of the Mt. McRae shales studied in (1). Based on fluid inclusion analyses, Haruna et al. (6) concluded that the fluids involved in processes that reached temperatures between 150°C and 200°C. Variable and negative δ56Fe values of diagenetic pyrites in the Archean black shales were, therefore, most likely caused by the dissolution/reprecipitation of pyrite (i.e., redox cycling of Fe), which was facilitated by locally discharged submarine hydrothermal fluids. This process must have greatly affected Fe isotope compositions of the pyrite crystals, which discourages the notion of Rouxel et al. that pyrite in the black shales recorded the Fe isotope signature of the global ocean at the time of black shale deposition. The δ56Fe variations in diagenetic/hydrothermal pyrites cannot correlate with the δ56Fe variation of Fe2+ in the overlying seawater.

Furthermore, diagenetic pyrites with negative δ56Fe values (as low as ~2‰) are actually common in modern marine sediments that accumulated under anoxic to suboxic water columns such as the Monterey, Santa Barbara, and Santa Monica Basins and the Baja Mats (7, 8). Yamaguchi et al. (9) previously noted the similarity in the δ56Fe values of pyrite between modern and Archean sedimentary rocks. Both the Fe and S isotopic compositions of syngeneic and diagenetic pyrite crystals in black shales likely represent only the local geochemical conditions of sedimentary basins and cannot be extrapolated to the global ocean.

Fourth, Rouxel et al. (1) propose that the δ56Fe values of pyrites in the ~2.3 to 1.7 Ga black shales became positive because they attained isotopic equilibrium with Fe2+ in the ocean water (δ56Fe = ~0‰). This is a poor argument, considering that they admitted in note 20 in (1) that “the fractionation of pyrite is poorly constrained from ~0.3 to 1.0‰ relative to dissolved Fe(II).”

To correctly interpret the Fe isotope data of pyrite and to better constrain Fe isotope geochemistry during sedimentary diagenesis, further experimental studies must be carried out to determine the equilibrium/kinetic fractionation factors among various Fe phases. Specific attention should be directed to observing Fe2+-aq, FeS, and FeS2 in various pathways during sulfide formation (i.e., Fe3+-aq → Fe2+-aq → FeS → FeS2) involving sulfate reduction, sulfide oxidation, and sulfur disproportionation reactions by microorganisms.

References
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Editor's Summary

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