

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

Olivier J. Rouxel,^{1*} Andrey Bekker,³ Katrina J. Edwards²

We reported a secular trend in iron isotope values of Precambrian sedimentary pyrite and related it to the changing redox state of Precambrian oceans. We restate that the iron cycle before 1.8 billion years ago was different from that now and reflected the rise of atmospheric oxygen and the subsequent moderate atmospheric oxygen level in the Paleoproterozoic.

Yamaguchi and Ohmoto (1) challenge our contention that $\delta^{56}\text{Fe}$ values of sedimentary pyrite from black shales reflect changes in the Fe ocean cycle in response to changes in the redox state of the ocean (2) and question our assessment of pyrite origins.

$\delta^{56}\text{Fe}$ values as low as -3.5 per mil (‰) are unknown from modern sedimentary pyrite but are common in Archean black shales. Their origin is best explained by the cumulative effect of Fe-oxide precipitation leaving the ocean with ^{56}Fe -depleted composition and further Fe isotope fractionation during pyrite formation. We therefore see no conflict with the estimates of Fe sink based on phosphorus adsorption on Fe oxides (3). Furthermore, these estimates are not quantitative because of uncertain isotope fractionation during pyrite formation and post-depositional effects on P/Fe ratios of Fe-rich sediments.

Banded iron formations (BIFs) are indeed stratigraphically above the black shales studied in each stratigraphic section, but Yamaguchi and Ohmoto (1) overlook three important points. First, we inferred that “Fe oxide deposition within marine sediments on continental shelves or in the deep ocean may have also provided an important sink for Fe between periods of large BIF deposition.” Second, deposition of the Mt. McRae Shale was preceded by deposition of BIF in the Brunos Band of the underlying Mt. Sylvia Formation (4). Finally, Walther’s law indicates that a conformable vertical sequence of black shales and BIFs implies their lateral equivalency. This has been documented in Western Australia, where shallow-water shales and carbonates of the Carawine Dolomite are time equivalents of the Marra Mamba BIF (4), and in South Africa (5).

Yamaguchi and Ohmoto (2) suggest that Archean pyrite nodules and, specifically, those of the Mt. McRae Shale reflect local diagenetic or hydrothermal conditions during their formation rather than overlying seawater composition. However, Haruna *et al.* (6) argued that hydrothermal activity occurred after pyrite nodule formation. The hydrothermal event is likely related to prograde metamorphism during the Ophthalmian Orogeny 2.21 to 2.15 billion years ago (Ga) (7). Multiple S isotope values of these pyrites are also inconsistent with hydrothermal origin. By analogy with S isotopes, dissolution/reprecipitation during diagenesis should have produced locally variable $\delta^{56}\text{Fe}$ values in pyrite nodules, which were not observed. In fact, $\delta^{56}\text{Fe}$ values of pyrite nodules from the same stratigraphic level are within 0.5‰ over the total range of 4‰ (1).

Yamaguchi and Ohmoto (2) also note that negative $\delta^{56}\text{Fe}$ values as low as -2 ‰ are common in modern marine sediments (8–10). Low $\delta^{56}\text{Fe}$ values of porewater (8), Fe-oxides (11) and pyrite (9) in these studies reflect diagenetic fractionation of Fe isotopes during redox cycling. Yamaguchi and Ohmoto (2) suggest a

similar diagenetic origin for Fe isotope fractionations in Archean and Paleoproterozoic pyrites. If negative $\delta^{56}\text{Fe}$ values of pyrite were indeed produced during sediment diagenesis by dissimilatory Fe reduction and pyrite precipitation, then complementary positive $\delta^{56}\text{Fe}$ values should have remained in the rock matrix. In contrast to this prediction, bulk rock $\delta^{56}\text{Fe}$ analyses of organic-rich shales, in which the Fe budget is not controlled by pyrite, yield $\delta^{56}\text{Fe}$ values similar to those of pyrite nodules (Fig. 1) in the same samples. Because Fe is a major rock-forming element in shales, changing bulk $\delta^{56}\text{Fe}$ values by diagenetic processes in sedimentary sections of more than 100 m thick appears unlikely. Negative $\delta^{56}\text{Fe}$ values as low as -2.3 ‰ were also found in bulk rock analyses of S-poor Archean open-marine shales of different ages by Yamaguchi *et al.* (10). Despite their assertion that modern and Archean Fe cycles are similar (10), these values are in marked contrast to those found in shales younger than 1.8 Ga, which are generally close to 0 ± 0.5 ‰ (10, 12, 13). Consequently, there is still no consistent or compelling evidence that supports a local diagenetic origin for negative $\delta^{56}\text{Fe}$ values of pyrites from black shales older than 2.3 Ga. Ironically, if measured $\delta^{56}\text{Fe}$ values were indeed produced during early diagenesis, one has to infer progressive change in global diagenetic processes likely due to the changing redox state of the ocean.

Fractionation factors involved in pyrite formation are indeed poorly known. Kinetic Fe isotope fractionation up to -0.9 ‰ during formation of greigite (Fe_3S_4), a precursor to pyrite, was recently observed (14) and might explain the positive $\delta^{56}\text{Fe}$ values after the rise of atmospheric O_2 through reservoir effects during sulfide precipitation. However, as cautioned in (1), the origin of positive $\delta^{56}\text{Fe}$ values in pyrite remains unclear, and further studies are required to elucidate the Fe biogeochemical cycle during the Paleoproterozoic.

Although the rise of atmospheric oxygen is now well constrained between 2.47 and 2.32 Ga, the redox state of the Precambrian ocean is still uncertain. Nevertheless, results obtained thus far show that before 2.3 Ga, shales have consistently negative $\delta^{56}\text{Fe}$ values for both pyrite and shale matrix, which are in marked contrast with their analogs after 2.3 Ga. The concomitant change of the Fe isotope record with other tracers of redox state of the atmosphere (15, 16) by ~ 2.3 Ga is best explained by a response of Fe ocean cycle to the rise of atmospheric oxygen.

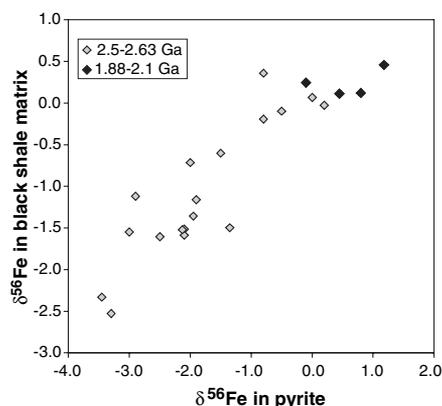


Fig. 1. Plot of $\delta^{56}\text{Fe}$ values of black shale matrix versus $\delta^{56}\text{Fe}$ values of associated pyrite nodules (1, 17). Black shale matrix was extracted from the area adjacent to pyrite nodules.

References and Notes

1. K. E. Yamaguchi, H. Ohmoto, *Science* **311**, 177 (2005); www.sciencemag.org/cgi/content/full/311/5758/177a.
2. O. Rouxel, A. Bekker, K. Edwards, *Science* **307**, 1088 (2005).

¹Marine Chemistry and Geochemistry Department, ²Geomicrobiology Group, Woods Hole Oceanographic Institution, Woods Hole, MA 02543, USA. ³Geophysical Laboratory, Carnegie Institution of Washington, 5251 Broad Branch Road, NW, Washington, DC 20015, USA.

*To whom correspondence should be addressed. E-mail: orouxel@whoi.edu

3. C. J. Bjerrum, D. E. Canfield, *Nature* **417**, 159 (2002).
4. B. Krapez, M. E. Barley, A. L. Pickard, *Sedimentology* **50**, 979 (2003).
5. C. Klein, N. J. Beukes, *Econ. Geol.* **84**, 1733 (1989).
6. M. Haruna *et al.*, *Resour. Geol.* **53**, 75 (2003).
7. B. Rasmussen, I. R. Fletcher, S. Sheppard, *Geology* **33**, 773 (2005).
8. S. Severmann, J. McManus, C. M. Johnson, B. L. Beard, *Eos* **84**, *Ocean Sci. Meet. Suppl.*, abstract O531L-09 (2003).
9. S. Severmann *et al.*, *Eos* **85**, *Fall Meet. Suppl.*, abstract V51A-0521 (2004).
10. K. E. Yamaguchi, C. M. Johnson, B. L. Beard, H. Ohmoto, *Chem. Geol.* **218**, 135 (2005).
11. M. Staubwasser, R. Schoenberg, F. von Blanckenburg, *Geophys. Res. Abs.* **7**, 09176 (2005).
12. B. L. Beard, C. M. Johnson, K. L. Von Damm, R. L. Poulson, *Geology* **31**, 629 (2003).
13. A. Matthews *et al.*, *Geochim. Cosmochim. Acta* **68**, 3107 (2004).
14. I. B. Butler, C. Archer, D. Vance, A. Oldroyd, D. Rickard, *Earth Planet. Sci. Lett.* **236**, 430 (2005).
15. J. Farquhar, H. Bao, M. Thiemens, *Science* **289**, 756 (2000).
16. A. Bekker *et al.*, *Nature* **427**, 117 (2004).
17. O. J. Rouxel *et al.*, unpublished data.

29 August 2005; accepted 14 December 2005
10.1126/science.1118420

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

Kosei E. Yamaguchi^{1,2*} and Hiroshi Ohmoto^{2,3}

Rouxel *et al.* (Reports, 18 February 2005, p. 1088) argued that changes in the iron isotopic composition of sedimentary sulfides reflect changes in the oxidation state of the atmosphere-ocean system between 2.3 and 1.8 million years ago. We show that misinterpretations of the origins of these minerals undermine their conclusions.

Rouxel *et al.* (1) recently reported the iron isotopic composition ($\delta^{56}\text{Fe}$ values) 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 Fe^{2+} in ocean water, whereas younger pyrites used the Fe from Fe silicates and Fe oxides buried in the sediments. (ii) The oceans were Fe^{2+} -rich and anoxic, and the atmosphere was anoxic before ~2.3 Ga. (iii) The oceans were stratified (Fe^{2+} -poor, oxygenated shallow water and Fe^{2+} -rich, anoxic deep water), but the atmosphere was oxidic 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 $\delta^{56}\text{Fe}$ values of Fe^{2+} that formed diagenetic pyrites became negative (−3.5 to ~0‰) as a result of the precipitation of very large amounts (50% to >90%) of Fe^{2+} as ^{56}Fe -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 Gamohaan Formations) deposited in basins before, not after, 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 $\delta^{56}\text{Fe}$ 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 these processes reached temperatures between 150°C and 200°C. Variable and negative $\delta^{56}\text{Fe}$ values of diagenetic pyrites in the Archean black shales were, therefore, most likely caused by the dissolution/reprecipitation of pyrite (i.e., redox recycling 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 $\delta^{56}\text{Fe}$ variations in diagenetic/hydrothermal pyrites cannot correlate with the $\delta^{56}\text{Fe}$ variation of Fe^{2+} in the overlying seawater.

Furthermore, diagenetic pyrites with negative $\delta^{56}\text{Fe}$ values (as low as −2‰) are actually

common in modern marine sediments that accumulated under an oxic to suboxic water column 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 $\delta^{56}\text{Fe}$ values of pyrite between modern and Archean sedimentary rocks [figure 11 in (9)]. Both the Fe and S isotopic compositions of syngenetic 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 $\delta^{56}\text{Fe}$ values of pyrites in the ~2.3 to 1.7 Ga black shales became positive because they attained isotopic equilibrium with Fe^{2+} in the ocean water ($\delta^{56}\text{Fe} = \sim 0\text{‰}$). 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 $\text{Fe}^{2+}_{\text{aq}}$, FeS , and FeS_2 in various pathways during sulfide formation (i.e., $\text{Fe}^{3+} \rightarrow \text{Fe}^{2+} \rightarrow \text{FeS} \rightarrow \text{FeS}_2$) involving sulfate reduction, sulfide oxidation, and sulfur disproportionation reactions by microorganisms.

References

1. O. J. Rouxel, A. Bekker, K. J. Edwards, *Science* **307**, 1088 (2005).
2. C. J. Bjerrum, D. E. Canfield, *Nature* **417**, 159 (2002).
3. Geological Survey of Western Australia, *Geology and Mineral Resources of Western Australia: Western Australia Geological Survey, Memoir 3* (Geological Survey of Western Australia, Perth, 1990).
4. South African Committee for Stratigraphy (SACS), *Stratigraphy of South Africa, Part I: Lithostratigraphy of the Republic of South Africa, South West Africa/Namibia and the Republics of Bophuthatswana, Transkei, and Venda* (Comp. L. E. Kent), *Geological Society of South Africa, Handbook 9* (Geological Society of South Africa, Pretoria, 1980).
5. T. Kakegawa, H. Kawai, H. Ohmoto, *Geochim. Cosmochim. Acta* **62**, 3205 (1999).
6. M. Haruna *et al.*, *Resour. Geol.* **53**, 75 (2003).
7. S. Severmann *et al.*, *Eos* **85**, Fall Mtg. Suppl., abstract V51A-0521 (2004).
8. S. Severmann, J. McManus, C. M. Johnson, B. L. Beard, *Eos* **84**, Ocean Sci. Mtg. Suppl., abstract O531L-09 (2003).
9. K. E. Yamaguchi, C. M. Johnson, B. L. Beard, H. Ohmoto, *Chem. Geol.* **218**, 135 (2005).

1 August 2005; accepted 7 December 2005
10.1126/science.1118221

¹Institute for Research on Earth Evolution (IFREE), Japan Agency for Marine-Earth Science and Technology (JAMSTEC), 2-15 Natsushima, Yokosuka 237-0061, Japan. ²NASA Astrobiology Institute, USA. ³Astrobiology Research Center and Department of Geosciences, The Pennsylvania State University, University Park, PA 16802, USA.

*To whom correspondence should be addressed. E-mail: kosei@jamstec.go.jp