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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.

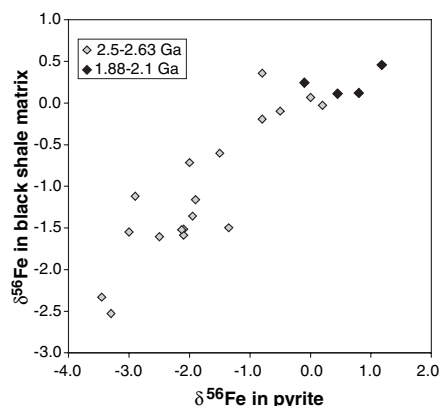


Fig. 1. Plot of $\delta^{56}\text{Fe}$ values of black shale matrix versus $\delta^{56}\text{Fe}$ values of associated pyrite nodules (1, 17). Black shale matrix was extracted from the area adjacent to pyrite nodules.

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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

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