

# Comment on “Abiotic Pyrite Formation Produces a Large Fe Isotope Fractionation”

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Guilbaud *et al.* (Reports, 24 June 2011, p. 1548) suggest that the geologic record of Fe isotope fractionation can be explained by abiological precipitation of pyrite. We argue that a detailed understanding of the depositional setting, mineralogy, and geologic history of Precambrian sedimentary rocks indicates that the Fe isotope record dominantly reflects biological fractionations and Fe redox processes.

Interpreting the origin of isotopic variations preserved in the rock record requires consideration of geologic, petrographic, and geochemical contexts. Guilbaud *et al.* (1) described a kinetic Fe isotope fractionation factor for abiological production of pyrite from aqueous and solid FeS, which potentially provides important insight into Fe isotope compositions of sulfides in the rock record. These authors suggest that negative  $\delta^{56}\text{Fe}$  values measured in pyrite from the geologic record could have been produced by this process, implying that Fe isotopes cannot be used to trace ancient biologically or abiologically mediated redox processes. We find such an interpretation to be faulty for three reasons: (i) The authors ignore evidence for biological and abiological redox processes contained in the diversity of Precambrian samples studied to date; (ii) the authors do not fully discuss the limited amount of low- $\delta^{56}\text{Fe}$  pyrite produced in their model; and (iii) the isotopic fractionations favored by the authors reflect extreme conditions produced in the laboratory and are unlikely to be representative of natural processes.

We first address the Fe isotope record for Neoproterozoic and Paleoproterozoic marine sedimentary rocks because it bears on the Fe redox processes that Guilbaud *et al.* (1) dismiss. Fig. 1A shows Fe isotope compositions of Fe oxides and Fe carbonates in banded iron formations (BIFs), Fe-rich shales, and Fe-rich and Fe-poor Ca-Mg carbonates. In all of these samples, pyrite Fe comprises <20% of the total Fe budget, and for most samples, especially BIFs, pyrite is insignificant or absent. The model proposed by (1) cannot, therefore, explain low- $\delta^{56}\text{Fe}$  values in such samples. Many Fe-poor, Ca-Mg carbonates have very negative  $\delta^{56}\text{Fe}$  values that have been interpreted to reflect the Fe isotope composition of a

marine photic zone with low amounts of aqueous ferrous Fe [ $\text{Fe}(\text{II})_{\text{aq}}$ ] after extensive Fe oxidation and precipitation of Fe oxide/hydroxides (2). The Fe-rich BIFs that were deposited coevally in the same basins have average  $\delta^{56}\text{Fe}$  values that provide sufficient mass balance to the Fe-poor Ca-Mg carbonate inventory, providing an example of an Fe redox couple (Fig. 1A). Indeed, as discussed in the references cited in Fig. 1, combining Fe isotope analyses with other geochemical evidence, notably carbon isotopes, indicates that the redox processes of microbial dissimilatory iron reduction (DIR) and Fe oxidation are likely means by which a >3 per mil (‰) range in  $\delta^{56}\text{Fe}$  values was produced.

We next turn to pyrite-bearing shales to test the relationship of  $\delta^{56}\text{Fe}$  and pyrite abundance predicted by the Guilbaud *et al.* (1) model. The model involves precipitation of ~10% of marine  $\text{Fe}(\text{II})_{\text{aq}}$  to form FeS, followed by reaction of FeS to pyrite; the maximum decrease in  $\delta^{56}\text{Fe}$  values for pyrite occurs when small amounts (<20%) of FeS are converted to pyrite, equivalent to ~2% pyritization of the initial marine  $\text{Fe}(\text{II})_{\text{aq}}$  inventory [~98% removal of  $\text{Fe}(\text{II})_{\text{aq}}$ ]. Such signals are unlikely to be found in bulk shales, in which much of the record of negative  $\delta^{56}\text{Fe}$  values in Precambrian rocks lies, because a negative- $\delta^{56}\text{Fe}$  signal for pyrite would generally be diluted by Fe-bearing silicates ( $\delta^{56}\text{Fe}_{\text{silicates}} \sim 0\text{‰}$ ). The low- $\delta^{56}\text{Fe}$  signal proposed by (1) would be most likely detected in rocks that have low total Fe contents and large proportions of Fe as pyrite and is possibly recorded in less than 10% of the samples plotted in Fig. 1B that have such a combination. In contrast, the numerous Fe-rich shales that have low proportions of their Fe inventory in pyrite and negative  $\delta^{56}\text{Fe}$  values (Fig. 1B) cannot be explained by this model. Additionally, virtually all of the measured low- $\delta^{56}\text{Fe}$  shales of Neoproterozoic and Paleoproterozoic age are enriched in Fe [ $\text{Fe}_T/\text{Al}_T$  greater than 0.5, the value of average Archean shale (3)], and there is no correlation between Fe enrichment,  $\delta^{56}\text{Fe}$  value, and the proportion of pyrite in the Fe inventories of these samples (Fig. 1C). Focusing on samples that have

>20% of their Fe inventory in pyrite,  $\text{Fe}_T/\text{Al}_T$ - $\delta^{56}\text{Fe}$  variations suggest the presence of pyrite that has a very low  $\delta^{56}\text{Fe}$  value (Fig. 1C). The fact that the majority of these rocks have  $\text{Fe}_T/\text{Al}_T$  ratios equal to or greater than that of average Archean shale suggests, however, that the low- $\delta^{56}\text{Fe}$  pyrite component is unlikely to reflect a process that occurred by the ~98%  $\text{Fe}(\text{II})_{\text{aq}}$  removal that is required by the model of Guilbaud *et al.* (1) and more likely reflects Fe addition. DIR has been recognized as an efficient “pump” for explaining net addition of low- $\delta^{56}\text{Fe}$  Fe to deep sections of marine basins [e.g., (4)].

Next, we turn to the experimental results obtained by (1). Guilbaud *et al.* chose an initial kinetic isotope fractionation for precipitation of FeS from  $\text{Fe}(\text{II})_{\text{aq}}$  that was measured for FeS precipitated over time scales of minutes to hours (5, 6), and the very large kinetic fractionation between FeS and pyrite they measured was obtained over periods of hours. Although many experimental studies indicate that pyrite can be formed rapidly, studies of modern marine environments indicate rates of pyrite formation that are orders-of-magnitude slower than those of laboratory experiments (7). Kinetically induced stable isotope fractionations can depend upon rates [e.g., (8)], and yet this critical point is not discussed by (1). Thus, we contend that the fractionation factors used by (1) represent laboratory conditions that may not be reflective of natural conditions, especially considering that 65 to 77% isotopic re-equilibration occurs between FeS and  $\text{Fe}(\text{II})_{\text{aq}}$  in 2 to 4 days at 25°C (9). Indeed, the lack of correlation in the experiments between percent pyritization and the measured Fe isotope fractionation factor [figure 1 in (1)] suggests that these data may largely represent experimentally induced kinetic effects.

We conclude that the Fe isotope compositions of Neoproterozoic and Paleoproterozoic marine sedimentary rocks are the result of numerous processes, including abiological and biological Fe redox processes. It is possible that some low-Fe samples preserve the signal proposed by (1), although their model is not a likely explanation for many low- $\delta^{56}\text{Fe}$  samples from the rock record, and their model does not address the temporal changes in the Fe isotope compositions of Precambrian sedimentary rocks.

## References and Notes

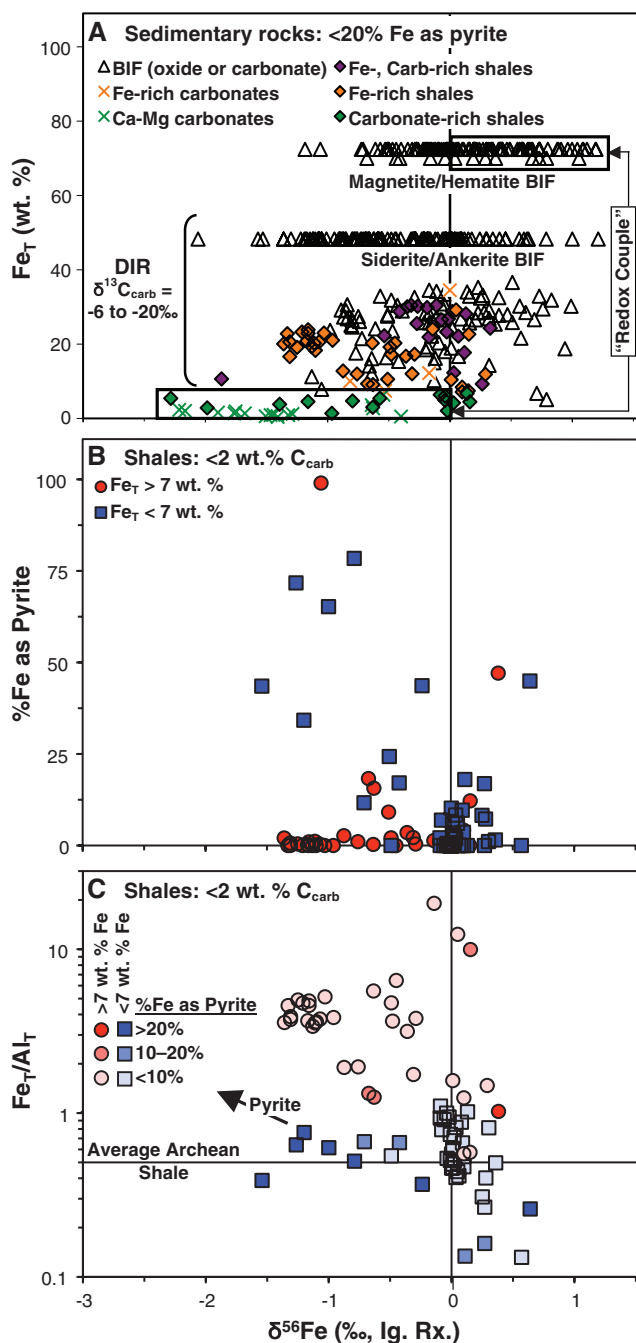
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**Fig. 1.** Fe isotope and chemical compositions of shales, BIFs, and carbonates of Neoproterozoic and Paleoproterozoic age.  $\delta^{56}\text{Fe}$  values are defined relative to the average of igneous rocks. **(A)**  $\delta^{56}\text{Fe}$  versus total Fe contents ( $\text{Fe}_T$ ) for various types of sedimentary rocks for which pyrite Fe comprises <20% of the total Fe budget. Magnetite and hematite BIF samples, as well as many of the siderite BIF samples (10–12), were collected from monomineralic layers, and thus their  $\text{Fe}_T$  values assume stoichiometries of  $\text{Fe}_3\text{O}_4$  (magnetite),  $\text{Fe}_2\text{O}_3$  (hematite), and  $\text{FeCO}_3$  (siderite) [72.4 weight percent (wt %) Fe, 70.0 wt % Fe, and 48.3 wt % Fe, respectively]. Total Fe values of all other samples (2, 13–15) were measured from bulk rock digestions. All samples are from the Hamersley and Transvaal basins. **(B)**  $\delta^{56}\text{Fe}$  versus the percent of Fe that is pyrite Fe for shales that have low carbonate contents (<2 wt %  $\text{C}_{\text{carb}}$ ). Samples that contain low- $\delta^{56}\text{Fe}$  pyrite formed by the model proposed by (1) would necessarily have low total Fe contents and a high percentage of Fe as pyrite (blue squares in the upper left region of plot) for such a signal to be detected in the bulk sample. All shale samples were analyzed as bulk rock digestions (2, 13, 14). It is important to note that the relations in Fig. 1B are cast in terms of percentage of Fe in pyrite, rather than the degree of pyritization, the latter of which references pyrite abundance to “reactive” (HCl-extractable) Fe, which may be problematic

because of alterations to the reactive Fe pools during even small extents of metamorphism. **(C)**  $\delta^{56}\text{Fe}$  versus the ratio of  $\text{Fe}_T$  to total Al ( $\text{Al}_T$ ) for low- $\text{C}_{\text{carb}}$  shales [the samples from (B) for which  $\text{Al}_T$  data are available] separated by the percentage of Fe that is pyrite Fe and by total Fe contents. These samples are shales that contain siliciclastic Fe, which will dilute any negative  $\delta^{56}\text{Fe}$  values contained in pyrite or other minerals (indicated schematically by the arrow). The  $\text{Fe}_T/\text{Al}_T$  of average Archean shale is that of Taylor and McLennan (3).



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