

Interactive comment on “Interpretation of kinetic isotope fractionation between aqueous Fe(II) and ferrihydrite under a high degree of microbial reduction” by Lei Jiang et al.

Anonymous Referee #1

Received and published: 21 June 2020

The authors aimed at determining the isotope fractionation factor of iron during the reductive dissolution of ferrihydrite by two different bacterial strains at two different pressures. The authors hypothesize that isotopic fractionation between Fe(II) and Fe(III) does not reach equilibrium when the sorption capacity of ferrihydrite for Fe(II) is reached and isotopic exchange becomes kinetically hindered. By this, the authors intend to confirm conclusions from Frierdrich et al. (2015) in the context of microbial iron reduction. Confirming these conclusions in a different context is valid but not highly innovative. Furthermore, Fe fractionation upon microbial reduction has been extensively investigated (see the multiple studies involving B.L. Beard, C.M. Johnston or E. Roden) so that is hard to identify knowledge gaps. In any case, the calculated fractionation fac-

C1

tors tend to increase over time in experiments with the largest extent of iron reduction. The authors compiled a nice data set. However, in my opinion, the data are not suitable to support a scientific publication due to the limitations to interpret them. This is the predominant reason why I propose to reject the manuscript. My concerns about the limitations are elaborated in the following. The authors use ferrihydrite in their experiments. As the authors realize, ferrihydrite readily transforms into secondary minerals in the presence of Fe(II) depending on, among other factors, Fe(II) concentration. Hence, it can be assumed that different types of secondary iron minerals have been formed in the experiments depending on the rates and extent of Fe(III) reduction. Changes in mineralogy, obviously, effect isotope fractionation and without quantitative information of the Fe isotope signature of the various Fe species it is very difficult to interpret fractionation factor. I also have several other concerns about the interpretation of the data: According to the methodology about 1 g Fh were added to 50 mL medium. This should yield a Fe concentration of about 120 mM. This implies that only around 50 % of total Fe was recovered, which questions the isotope values for Fe(III) when the digestion was not quantitative. The trend that Fe recovery decreases with progressing reaction might reflect Fe mineral transformation (e.g. magnetite formation). The ratio $\text{Fe(II)}(0.1\text{M HCl}) / (\text{Fe(II)}(0.1\text{M HCl}) + \text{Fe(II)}(0.5\text{M HCl}))$ exceeds 0.25, which is larger than a realistic concentration of surface sites (about 0.2 per Fe for HFO). This implies that not all extracted Fe(II) is adsorbed Fe but includes structurally bound Fe(II). The authors do not mention anything about pH. Does the pH change throughout the reaction (no buffer is present in the medium) and how would pH effect fractionation. Considering these uncertainties, I am sceptic that the data set could be used to rigorously discussing fractionation mechanisms or deriving reliable fractionation factors. I have also a couple of minor comments: Why did the authors vary the pressure? The experimental design is not justified. Varying the reduction rates or manipulating the Fe(II) / Fe(tot) ratios could have been easier achieved by adapting the bacteria / Fh ratio. Using different organisms and pressures creates unnecessary ambiguity. Fh is produced by neutralizing a Fe(III) NO₃ solution with KOH. The authors do not mention any purification step before

C2

freeze drying, implying that the solid should contain considerably amounts of nitrate. I presume the organisms can both use nitrate as electron acceptor or not? What would be the implications of the presence of nitrate.

Minor text related comments The first two sentences in the abstract do not help to grasp the content of the study but obscure the subject. My first impression was that the authors argue that isotopic fractionation is the cause for the cessation of iron reduction. Line 37, I presume the final rates were only a few percent of the initial rate (reformulate).

Interactive comment on Biogeosciences Discuss., <https://doi.org/10.5194/bg-2020-85>, 2020.