

Interactive comment on “Technical Note: Uncovering the influence of methodological variations on the extractability of iron bound organic carbon” by Ben J. Fisher et al.

Anonymous Referee #3

Received and published: 30 November 2020

The manuscript is an extended footnote to an earlier paper Fisher et al. paper published this year on the effect of organic acids on reactivity and solubility of iron oxides. The manuscript addressed three aspects of a modified citrate-dithionite-bicarbonate (CDB) extraction method used for determining Fe content associated with various iron oxide mineral phases. Variables tested were the dithionite concentration, freeze-drying versus wet extraction, and time of extraction.

Starting with the title, the goal of the study and the actual study is mismatched. The paper is about extraction of iron oxides, and the entire discussion revolves around the efficiency of the dithionite method toward the extraction iron oxides at circumneutral

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pH, not the organic carbon that is extracted. My reading of the Lalonde et al. 2012 article is that they were employing a more gentle (i.e. circumneutral pH) treatment in order to not overestimate the loss of organic carbon due to hydrolysis. That is perfectly reasonable, as they did not want to overestimate OC losses from the main pool due to hydrolysis. Their goal was not to accurately quantify the Fe content, but to dissolve most of the iron oxide fraction and thereby release iron oxide bound organic matter. Here, the authors imply that this approach is not quantitative.

It is not clear at whom or at which samples this study is aimed. The authors only considered ferrihydrite. So is this applicable only for modern sediments? What about sediments or rocks containing greater concentrations of goethite or hematite?

The authors claim that no study has thus far has performed a determination of the reductive capacity of the dithionite method (Lines 74-75). The authors, however, also do not clearly provide the criteria for “reductive capacity”. It is only implied in their approach of using varying “weight percentages of OC-Fe” that simulates a titration of sorts. And as described below, there are methodological problems with this approach.

It is not clear that this a substantial step beyond the Fisher et al., 2020 paper. The authors pose the question of whether there is a one-size-fits-all solution (line 95), or should the extraction be adjusted to fit the set of samples and exact research question. But they do not really answer this question. For instance, the effects of freeze drying on wet chemical extractions of sediments as extensively discussed in Section 4.2, has long been known (e.g., Rapin et al., 1986, ES&T; and more recently Raiswell et al., 2004, Chem Geol.). This discussion is superfluous. The authors point out the problems faced by every sediment biogeochemist, but offer no new insights of their own, or at least none that have not been already considered by other studies. They propose no solutions to any of these aspects, except to say that methods employed should be rigorously documented. As the authors point out, analyzing freshly collected wet sediments is not practical for most studies. One has to ask if the efforts to improve the dithionite method are even worth the effort, if freeze-drying is out of the question.

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The topic of study is an important one in sediment biogeochemistry, especially in how do we deal with examining organic carbon concentrations and speciation in complex matrices. But does this paper bring about a consensus on how to proceed? Unfortunately, I have to answer, no it does not, outside of stating that when using wet chemical sediment extraction methods, that geochemists should carefully consider the type of sediment being analyzed, the amounts of reactants in the methods, sample storage and the exact question being investigated.

Methodology

The high iron oxide contents used in these experiments are problematic. First of all, it is not entirely clear what exactly is being measured (see comments on the term “OC-Fe”). Let’s assume that it is %Fe. For example, the 20% OC-Fe sample contains 0.2 x 0.25 g artificial sediment, or 0.05 g Fe. In the 15 mL of reaction solution, this gives ca. 0.06 mole/L Fe. The dithionite solution of 0.25 g Na₂S₂O₄ in 15 mL yields 0.093 moles S₂O₄²⁻ anion per L. Assuming that upon disproportionation of the dithionite in water yields two reducing equivalents, which is probably overestimated due to side reactions with oxygen and other S decomposition products, we would have <0.18 mol/L dithionite reducing capacity. Dithionite is barely in excess of the reactive iron fraction, which is a poor starting point for a quantitative extraction. It certainly becomes worse or untenable at 50% or 75% or 100% OC-Fe contents. If the OC-Fe weight% refers to FeOOH, things improve. But only by a third. It is not surprising that the method fails to reduce these high Fe oxide containing slurries. These high Fe concentrations are actually not realistic (see also my comment below). As the authors point out in Line 259, wt% Fe contents in most sediments are usually less than 10%.

The high iron concentrations used in these experiments exacerbate another problem with the experimental set-up. As far as I can tell, the samples were not shaken. I assume that the precipitates sank to the bottom of the reaction vessel (details on the reaction vial type and geometry are missing). Over time the reaction rates will become diffusion limited without shaking. This also renders the results of the time-course

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experiment somewhat difficult to interpret.

There appear to be no replicates for each dithionite addition. This makes interpretation of the results, especially in Figure 2, difficult.

Style and Readability

The manuscript would be better served by a radical reduction in length. This is a technical note describing three relatively short comparison experiments that are an extension of the Fisher et al. 2020 paper. For instance, the first two sentences of the manuscript (lines 25 to 27) are obvious to readers of Biogeosciences. There are details (Lines 166- 174) about diluting samples for AAS analysis that do not need to be repeated in such detail. The reader assumes that the authors have a basic understanding concerning the basics of the instrumental analysis. Section 2.7 appears superfluous because there is no where in the Results where organic C is discussed.

On the other hand, the any clear description of the carrier material was lacking, and I had to read the Fisher et al. 2020 Chem Geology article to understand how this key component had been treated.

I am confused by the use of the term “OC-FeR”. What exactly is this? Organic C associated with iron oxides, as per Lalonde et al., 2012? Or is this Fe that is somehow made unreactive by Organic Carbon? Or is this simply the total iron oxide content? Or perhaps, the reactive iron content, whatever that may be? Are they referring to %dry weight Fe? Or are they referring to %dry weight FeOOH, or perhaps Fe₂O₃?, or perhaps %weight of whatever happens to precipitate including the organic fraction added?

Further Comments

Line 183 The clause in the first line of the Results has no meaning. The manuscript is plagued by ill-defined discussion of reactivity. There are sentences such as “associated OC has a large influence on Fe reactivity.” Towards what?

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Line 65: This sentence is misleading. Many permutations, improvements and evaluations to and of the dithionite method have been made, particularly with respect to marine sediments. See for instance Lord 1982 (J Sed Petr.), Kostka and Luther 1994 (GCA) and Raiswell et al. 1994 (Chem Geol). The authors must be referring to the extraction of organic matter. Line 46: This is not surprising as hematite has been shown to be only partially dissolved by CDB method (see Kostka and Luther, GCA, 1994).

Line 48 What do the authors mean by Fe reactivity here? Is this the goal of the study? Or the extractability of organic compounds.

Line 54 “developed” knowledge?

Line 120 This is not a concentration gradient. First of all, the authors are referring to contents, not concentrations (there seems to be confusion about the terms concentration and content throughout this manuscript). Secondly, a gradient implies a change in concentration over some property (e.g. depth, distances, density, etc..)

Line 122 Confusing. Was the carrier material freeze-dried before or after mixing (or not all)?

Line 140 This is repetition of the Lines 80 and following.

Line 170 Samples that were highly concentrated were diluted only 10 times while the more dilute samples were diluted 20 times?

Line 180 It's not clear that the authors differentiate here between a standard that is used for calibration and a secondary standard used as control.

Line 190: This does not show the reductive capacity of the dithionite. If, for instance, dithionite is in excess, then 100% Fe extraction cannot show the reductive capacity of the dithionite.

Line 224 Freeze-thawed samples? This experiment is not mentioned in the methods. Furthermore, this sentence (which is also discussion/interpretation) does not make

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sense. What “previous one”. The sentence refers to Figure 1. There are no freeze-thaw or freeze-dry samples in Figure 1.

Figure 1: What do the fits represent and how is the fitting done? It looks to me like if you added more dithionite, eventually the %Fe recovery would start to decrease at some point. Also, the blue symbols representing maximal Fe extraction do not match the corresponding curves for the black symbols.

Figure 2 is difficult to interpret. Firstly, the dependent variable is plotted on the x-axis, which is confusing for the bar chart depiction. Secondly, outside of the observation that freeze-dried sediments tend exhibit lower extractability than the fresh samples at high Fe contents, it is difficult to ascertain any kind of trend. Given the lack of replicates for each sample, and the large degree of variability in extractabilities, I find it difficult to be able to say anything concrete about these results.

Line 215 : “Typically”?

Line 251: Repetition.

Line 261. This is a red herring type of argument. One of the reasons that sediments are dried or freeze-dried and ground, is to avoid the problem that very small sample sizes and heterogeneity incur in solid phase analytical chemistry, when comparing average samples within a study. If one is interested in very small scale Fe-C heterogeneity, then a wet chemical extraction method is not the right approach.

Line 284: Confounded?

Line 284: Just state that the reagents were no longer in excess (see comments above).

Line 294: I don't believe that the authors mean to say that organic carbon is reduced and released into the solution phase. Interestingly, sulfite incorporation into carbonyl groups may promote organic carbon solubility.

Line 303: If increasing reagent additions make more problems, then what is the point?

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Line 399: There is no “standard” method against which to calibrate.

Interactive comment on Biogeosciences Discuss., <https://doi.org/10.5194/bg-2020-399>, 2020.