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Discussions

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.

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Fisher et al. present results of experiments into the extractability of OC-FeR (that is to say, sedimentary organic carbon bound to reactive Fe) during treatment with citrate-bicarbonate-dithionite solution. CBD extractions are a commonly applied method, either stand-alone or as part of sequential extractions, for investigating elements associated with reducible phases in marine sediments. As the authors state, there is much heterogeneity in the details of applied CBD extraction protocols, even within the narrower context of studies into OC-FeR. This has led to difficulty in comparing results and the possibility that the currently used protocols may be sub-optimal for their

stated goals. Therefore there is clearly a need for studies like this one, to eventually improve/harmonize the approaches used in the community.

Overall I had the feeling that the study delivers some interesting results although some of the interpretations are left only lightly justified. This leads to the idea that a more developed set of experiments could have yielded a more useful step forward. For example, the conclusion that complexation by citrate may be limiting the recovery of Fe in the highest-OC-FeR experiment deserves to be tested through a concentration series similar to the dithionite series the authors report. This is especially the case considering the comments of the first reviewer (Henkel) questioning whether citrate limitation is a feasible explanation for the observations in Fig. 1. I do not demand that the authors produce such additional data before publication but it is clear that their conclusion would be more robust if it was available, and therefore the overall impact of the study would be greater. A similar criticism could be leveled at the interpretations of the experiment comparing freeze-dried and wet samples, although I would say this is a complex topic that warrants a separate study.

Another important point is that it seems that some of the content here may be an overflow from the authors' recent Chem. Geol. paper (cited Fisher et al. 2020), which is not a criticism as such but in some cases I had the feeling the reader is being referred there to explain what is going on in the experiments presented here, which should be avoided as this ms. must also be a stand-alone study, even if it is a Technical Note. I am specifically referring to the interpretation of the results of the experiment in which the degree of carboxylation of OM in synthetic OC-FeR is varied (Fig. 2). The discussion of the mechanisms here (Paragraph from Line 358) is too thin and the reader cannot understand why the degree of carboxylation makes such a difference to Fe extractability without accessing the other paper.

Unfortunately I read Susann's review only after making my own comments on the original ms., then later noticed that she has done a very comprehensive job and found several of the same issues that I wished to highlight. It is good to see that the authors

have responded thoroughly to Susann's comments and this will undoubtedly improve the next version. Therefore my list of additional comments is comparatively short.

General (in addition to the above; all Line numbers refer to the original ms):

- The Introduction can be better worded and arranged: First I suggest to move the para. starting Line 59 to directly above the short para. starting Line 81. This way you first describe the problems with the existing methodologies, then set out how you intend to solve them. Next, check a few key sentences: e.g. Line 26 "Understanding in which environments organic carbon (OC) persists": please clarify that you are referring to preservation of OC in sediments; Line 54 "fully reduce all solid reactive Fe phases and associated carbon"... I could not find this phrase in Lalonde et al. 2012, although it is presented here as a quotation. Please check.

- Throughout: the terminology in this field is easily misunderstood. E.g. the first reviewer thought for the whole time that % OC-FeR refers to % of total sediment, when in fact it refers to % of total OC. I also had major difficulties to get this upon first reading. So I suggest to clarify terminology early on, and modify figures and captions to make this easier to follow. E.g. I note that Barber et al. 2017 use more descriptive terminology in tables and figures e.g. "OC bound to Fe (% of total OC)" in their Table 1 and "Fraction of total sediment Fe" in their Fig. 4. Also check that CDB/CBD is used consistently. Both current appear.

- Description of Fig. 1 results. The phrase "maximal extraction" is used repeatedly when describing the results, but it is only explained in the Discussion (Line 266). The best place for this description is actually Methods, because you can already state how you intend to use the data to estimate this value. That will make reading the paper a whole lot easier overall.

Specific

- Line 67: maybe qualify with 'partial hydrolysis' or similar. For significant digestion of

OC from sediments, either very low pH (and use of specific oxidizing acids) or very high pH are required.

-Line 89: misplaced comma after "suggesting"

-Line 111: "and" should be "a"

-Line 120: "varied" in preference to "differed"

-Line 192-193: rephrase to "with those samples containing the least Fe showing the greatest proportional/relative extraction of Fe"

-Line 203-205: this looks more like part of a caption for Fig 1

-Line 244-246: Does this mean that the natural sediment samples in these experiments were freeze-thawed before the experiments? If so it will be important to state this in Section 2.2.

-Line 251: why give the formula? there are many Fe oxides that can be dissolved in dithionite so I suggest just to leave it out

Line 259-263: Not clear how XAS can indicate clustering. If you are referring to locally enhanced concentrations ("hotspots"), yes this is a real phenomenon observed by high-resolution mapping techniques. Still, I would be surprised if a homogenized sample of 0.25g would have a distinctly different OC-FeR content from the bulk sediment, so the logic of the statement is not clear and the paragraph does not really benefit from it.

Line 293-294: This is a confusing opening sentence to the paragraph. Rephrase to make more concise.

Line 304-305: It is not clear to me how an increase of DOC (citrate) during the extraction would impact on the quantification of OC after the extraction., if this is done on the solid phase. Can the sample not simply be rinsed before the drying and analysis?

Line 326-328: Clauses of the sentence are not well constructed