

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.

Peter Kraal (Referee)

peter.kraal@nioz.nl

Received and published: 2 December 2020

Review of bg-2020-399

With interest I have read this manuscript, in which the authors explore the impact of adaptations to an established chemical method (reductive dissolution of Fe(III) by dithionite) to extract OC associated with Fe oxide minerals. This topic is of interest, because the impact of Fe-OC interactions have a bearing on the environmental fate (and possible global budgets) of both Fe and C. However, the manuscript seems to imply that no adaptation is necessary for the majority of marine sediment samples, and the full analytical impact of some suggested changes was in fact not explored. As such, in my

C1

honest opinion, I do not really see the added value of this “technical note”. I do not think that the rather loose suggestion, that increasing dithionite concentration during OCFe extraction might be useful with the caveat that it may have negative consequences that were not investigated, is particularly useful to the geochemical community. Furthermore, I think that the authors overlook some key points that can be taken from the data and do not properly consider the relationships between the findings for the poorly ordered synthetic Fe(III) precipitates (and their properties) and natural samples. Below are detailed comments.

Note: I prepared this review and afterwards read the excellent, extensive reviews by Susann Henkel and Tom Jilbert. I apologize for a limited degree of overlap.

Key points

General language: unnecessarily verbose and at times rather vague, essentials are buried in winding sentences from which the reader has to deduce the actual information. For a technical note, the experimental section is poor.

There seem to be some errors in the use of % and wt.% which are a bit confusing, please carefully check units for Fe and OC concentrations and extraction efficiencies.

Regarding the choice of organic compounds, I understand why the selection was made to have compounds with different amounts of carboxylic functional groups. It would be good if the authors could also explain the choice for these compounds in general, from a point of view of representing natural organic material in marine sediments. As mentioned by Tom Jilbert, the discussion on the impact of type of organic compound (L358 ff) is weak and too dependent on other study by Fisher et al.

Coprecipitation is known to affect the structure of Fe(III) precipitates, was any mineralogical characterization of the Fe(III) precipitate performed? The impact of coprecipitation will perhaps be minor for 2-line ferrihydrite, i.e. a poorly ordered Fe(III) precipitate would likely become a bit more disordered. However, there are indications

C2

that such minor changes in structure can result in large changes in reactivity (and thus solubility). And the very high OC:Fe ratio might in fact result in a Fe(III)/OC coprecipitated that is not 2L ferrihydrite but some organic-rich, amorphous hydrous ferric oxide. There is no mention or discussion on the likely characteristics of the Fe(III) precipitates and their relation to natural counterparts anywhere in the paper.

Also, I wonder why only 2-line ferrihydrite was used? This poorly ordered Fe(III) precipitate often transforms very rapidly into more crystalline Fe(III) precipitates such as lepidocrocite or goethite (for which limited solubility in CBD would be much more relevant?). Overall, it would be good if the authors could spend some words on their exclusive choice for 2-line ferrihydrite (or the Fe(III) precipitate that would actually form under the experimental conditions): is it representative for the Fe-OC pool in soils and/or sediments?

Would have been interesting to see OC extraction efficiency for all treatments with the Fe-OC/sediment mixtures, not sure whether results from the variable dithionite experiment justifies assuming 1:1 relationship between Fe and associated OC extractability across the experiments conducted in this study. In fact, it would have also been very useful to have OC data for the dithionite/FeOC concentration range in the first experiment shown in Fig. 1: currently, we are not really given much to go by to understand how OC extractability varies as function of extraction conditions: one number for OC and then the assumption that Fe extractability is a perfect proxy for Fe-associated OC extractability for synthetic precipitates and natural samples alike. I find this a bit meagre (particularly for a technical note).

The impact of freeze-drying (section 4.2) is not represented properly. It shows a strong negative effect on the extractability of synthetic fresh Fe(III) precipitate, which is to be expected and reported regularly for poorly ordered Fe(III) precipitates (e.g. Kraal et al., *Chemosphere*, 2019). But is showed to have no effect on Fe extractability from the Arctic sample! However, in the discussion this important observations is ignored and there is a winding, unfocused and partly incorrect (see also Susann Henkel's review)

C3

discussion on the practices and challenges of freeze-drying. I have some reservations about the discussion on the impact of dithionite concentration on extraction efficiency in relation to increasing concentrations of Fe and OC. Firstly (L273-281), the authors present data from sediment/synthetic Fe-OC mixtures with Fe and OC concentrations that are incredibly high and as far as I know definitely not, as the authors claim, common (20-30 wt% OC and > 10 wt% Fe are not representative of normal marine sediments, shallow or deep). Secondly, the authors focus a lot of attention on the relationship between dithionite concentration and OC content (L272-281), while I would expect that it is the ratio between dithionite and Fe (which is discussed later in the discussion, L282-291). I would argue that the bulk OC content of a sediment has relatively little to do with extractability of OC-FeHR, and I think this discussion on the role of dithionite concentration should better reflect the processes by which OC-FeHR is liberated. It actually seems like the "standard" (Lalonde) procedure works well for most sediments. The only adaptation really put forward in the current technical note is increasing the dithionite concentration, with two huge caveats: it seems only necessary for extremely Fe-rich samples (an observation not properly represented, as mentioned above) and the authors suggest that jacking up the dithionite concentration may have negative consequences on the performance of the extraction method, without actually exploring those potential negative impacts. I then wonder what to take away from this technical note?

Detailed

L29. CO2

L87. HCl

L100-115. Would be nice to report the Fe/OC ratios during coprecipitation and the rationale behind choosing the concentrations. Also, how long was the precipitation allowed to occur? L111-112. a factor

L113. binding association? Seems repetitive. It's also not type of binding, as all organic

C4

compounds have carboxyl groups. So... do you mean denticity, i.e. number of groups with which ligand binds to atom?

L112-115. Please rephrase this, it is unclear (what is "weak" binding in this context?) and the link to slurry and dry sample is not explained.

L117. "to explore whether mechanistic trends persisted", please explain what this means here. In other words, use less fancy words and provide more concrete information about what you want to test by varying Fe-OC content

L119. "using the same original carrier sample and similarly treated to liberate OC and inorganic carbon". You mixed marine sediment with your Fe-OC precipitate (I think that 'carrier' terminology is both unnecessary and incorrect as a carrier is strictly something else than a matrix). What does "the same original carrier sample" even mean, you used the same sample as used by others before? And can you please better explain what treatments were applied to the sample, rather than "similarly treated to liberate OC and inorganic carbon", which could mean treatment for IC and OC was similar, or it was similar to treatments by Fisher et al. You are not writing a novel, the reader expects a clear and concise (and correct) description of materials and methods applied to them. So, as matrix (I am not adopting the 'carrier' terminology) you used sediment from which CaCO₃ and OC were removed, right? L121. Why "spiking" here and "mixing" before?

L136-137. Was the artificial seawater deoxygenated? Do you expect any Fe precipitation issues when introducing oxygenated seawater into a sample with Fe(II)? Also, what was the composition/recipe of the ASW? Wash steps commonly involve simple strong salt solutions (e.g. 1 M MgCl₂), preparing ASW for this seems like an extra step for which I would like to know the rationale.

L140. "Testing the impact of different extraction conditions"

L162. What is freeze thawing? Just thawing?

C5

L174-184. Only after reading section 3.1 does it become clear in which samples OC was measured. Please rewrite/rephrase this section, the whole thing is difficult to understand. In particular, sentences like "Carbon content was not measured for all samples, but was used [used?] during the experiment where Na dithionite concentrations varied (see section 3.1)." and "This was performed to ensure that at the end point samples with incomplete Fe recovery also experienced incomplete OC recovery, as expected due to the <1 OC:Fe molar ratio of our coprecipitates." are awkward because they do not concisely convey the relevant information but rather circle around the relevant information with winding sentences. So, why do you expect correlation between Fe and OC extractability based on the OC:Fe ratio? If it's a coprecipitate, this correlation is expected irrespective of the ratio? To be blunt, the writing style is verbose, rather vague and indirect, which is really taking my attention away from the relevant information (which I have to deduce myself in part). Lastly, in light of the considerable and inconsistent differences between Fe and OC extractabilities, I would actually have been interested in OC extraction efficiency for all the different treatments, I do not really understand why these data were not included, I am also not convinced that the results for one type of experiment (varying dithionite concentration) justify using Fe as only indicator of Fe-OC extraction efficiency across a range of experiments.

L186. So, the first thing I am interested in, is the composition of the Fe-OC precipitates. Is all the OC coprecipitated; did any Fe or OC remain in solution after the precipitation reaction? Also, the 'concentration range' was based on mass% of Fe-OC in the sediment/Fe-OC mixtures, but it is unclear what the concentrations of Fe and OC were in these mixtures (only in L200-201 is this addressed for the first time I think). 20-50 wt% seems biased to really high concentrations of Fe-OC where extraction efficiency is actually low, curious to know why this range was chosen. So, please start the Results section with information on the precipitates that were synthesized, and in the Materials and Methods talk a bit about the choice for the concentration range.

L186. The key is Na dithionite concentrations in solution rather than quantities, I would

C6

say.

L189. Added to the solution, not “our reaction”

L190. Maybe good to immediately emphasize this is a Na dithionite test using the Fe-OC/sediment mixtures in the text, not only in the Fig. 1 caption. Also, mention which OC source (1, 2 or 3 COOH) was in the coprecipitates used for this test. By the way, is the blue axis title correct? “Maximal OC-FeHR extracted (wt%)”? Is the unit wt%, or % of initial OC-FeHR?

L190-191. I object to “this figure can be interpreted as a visualisation of the reduction capacity of Na dithionite relative to initial Fe content”. The reduction capacity for me is determined by the cell potential for the redox reaction. The plot shows a decreasing Fe reduction efficiency with decreasing initial dithionite/Fe(III) ratio.

L196. baseline dithionite addition?

L203-205. There is a blue triangle that does not correspond to anything in the legend. Also, using OC-Fe as name for Fe-associated OC is very confusing (to me, OC-Fe would imply OC-associated Fe just like FeS₂-Fe means pyrite-iron), please address this and use unambiguous names for the extracted Fe and OC.

L205. “within 10%” is a bit misleading here, because it is the absolute error so in a relative sense it becomes bigger, > 10%, at lower extraction efficiencies, please address this. L206. At which dithionite concentration?

L208. “varying C content” is highly confusing here, you mean three types of OC, right?

L207-212. I am confused again. From the methods (section 2.1), I gather that the Fe-OC coprecipitates used in the dithionite concentration experiment reported in Figure 1 contained hexanedioic acid (‘2 COOH’) and was performed with freeze-dried Fe-OC. In Figure 1, it shows a decrease in % Fe (and presumably % OC) extracted with increasing Fe-OC wt% from 90% to 40% between 20wt% to 50 wt% Fe-OC. But in Fig. 2, Fe extraction % decreases from 50% to 30% for 20 wt% to 40 wt% Fe-OC for freeze-

C7

dried Fe-OC with 2 COOH as C compound. Am I misunderstanding something, or was there a big difference in Fe extraction % for the two experiments under supposedly similar conditions? As an aside, it would be very useful if the authors could mention at which dithionite concentration the second experiment was conducted (maybe it is tucked away somewhere in the Materials and Methods, please repeat in this section).

L215. With 2 out of 5 treatments not showing this trend, I would consider removing “typically”.

L219-220. What is implied here? The sediment contains 20 wt% Fe-OC, that is not a trace amount where analytical limitations would interfere with trends (it is mentioned earlier that this is equivalent to 7 wt% easily reducible Fe). Please explain how the comparatively low (emphasis on comparatively, as the whole range is strongly biased towards really high Fe-OC concentrations) Fe content could obscure a trend.

L224. “were extractable for”? Please rephrase.

L225-227. No doubt this will be dealt with in the discussion (having read the discussion, I now know it is not addressed), but there is a large difference of the impact of freeze-drying on freshly precipitated poorly ordered Fe (for which it is established that freeze-drying decreases reactivity, likely by aggregation) and natural sediment from a depth of 22-23 cm in the sediment in which you will not find any labile, freshly formed Fe unless the sediment forms fresh minerals as an artifact of sample treatment (or am I wrong? There is in fact no information on the chemistry of the studied sediment at all). In this sense, there seems to be a mismatch between the synthetic sample and the natural test material.

L230. “labile” sediment?

L231. Extraction time was extended in 15 min increments

L233. remains constant

L239. So there is the issue of OC hydrolysis at low pH. But to quantify OC in sediments,

C8

they are commonly decalcified to remove inorganic C, using dilute HCl. What do the authors think about this? Does low pH have to be avoided at all costs during CBD extraction, to then submit the sediment to low pH during decalcification?

L239. You targeted physical aspects? Such as... the concentration of dithionite??? This is chemical, surely.

L244-246. As mentioned before, the authors should probably also consider the large difference between the impact of freeze-drying on freshly coprecipitated Fe/OC and the impact of freeze-drying on relatively old and stable sediment. I do not think these are comparable.

L258. Is the unit wt%? The context implies that this is the recovery efficiency (% of added Fe that is subsequently extracted), not the Fe content in the sample. (Should be checked in other instances as well, for instance y-axis of Fig. 1)

L268. "is removable for"?

L271-281. Because Fe and OC co-vary in the treatments, it is hard to judge what factor determines decreased extractability of OC-FeHR: is it the increase in OC or the increase in Fe (up to 24 wt% Fe!)? Merely looking at the trend in OC-Fe extractability in Fig. 1 does not answer that question. I would expect OC-FeHR to be liberated by dithionite because the Fe is reductively dissolved, and so the efficiency of OC liberation scales with efficiency of Fe reduction and not necessarily OC content. This would in fact mean that the bulk OC content of the sample is irrelevant, and the focus is on the wrong parameters in this section. The text in L293-306 supports this, the authors need to rethink their focus and wording here to better capture the chemical processes that occur when treating a sample with dithionite to reductively dissolve FeOx and associated compounds/elements. Again, regarding the units: the concentrations should probably be wt.% rather than % for the reported OC-Fe contents? Also, the authors mention that "many samples exist in the 20-30 [wt.]% range". And "the average value for marine sediment OC-FeHR composition is greater than 20 [wt.]%". These num-

C9

bers and statements surprise me. Studying coastal and deep-sea sediments myself, I usually find TOC concentrations of 1-10 wt.% in a range of marine environments. The authors seem to claim that extremely organic-rich sediments are in fact very common (even though the phrasing "in many samples" is very different from "in many marine systems"...), and then provide just one example, one value, from the Equatorial Pacific. I would like to have this point discussed a bit more: what kind of depositional environments host these very OC-rich samples, are we talking about modern or ancient (black shales and such, where the issue again appears that testing with labile OC-rich HFO makes little sense)?

L293-306. So, now the authors are saying that the existing method works fine for most samples, that increasing the concentration of CBD could work for some (extreme) samples but may also have negative effects that are not explored... So what are we to do with this technical note?

L307-367. This is an excessively lengthy paragraph on freeze-drying. It is actually strongly detached from the findings and just meanders along various aspects of freeze-drying. The main issue is that the authors do not correctly represent their own results: a decrease in Fe extractability was found in the synthetic samples, but not in the Arctic samples! As I mentioned before, it is to be expected that freeze-drying a much stronger effect on a fresh, poorly ordered Fe(III) precipitate than on a rather old sediment sample. In fact, there are findings that show that freeze-thaw cycles can increase extractability of elements (the authors also touch upon this, and Susann Henkel also hints at some inconsistencies in this section). Note: this is a change in extractability, not content; the text became rather confusing when the authors started to speak about freeze-drying as a treatment that can increase the contents of for instance OC and metals... (L351-353). Overall, this whole section fails to address the key point, i.e. the discrepancy between the results for the synthetic and environmental samples (or, in broader terms, the difference between artefacts in fresh and old Fe minerals, whether they are synthetic or natural), and instead presents long and rather unfocused and at

C10

times confusing literature review on freeze-drying.

Despite my sharp tone (work in progress), I trust this review is fair and constructive.

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