Response to review by Anonymous Reviewer 3.

Original comments in black, response in blue.

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.

We thank the reviewer for their review of our manuscript. On the point that they feel this is an "extended footnote", it may be useful for us to clarify the differences between our previous study and this new submission for any readers unfamiliar with the earlier work. The reviewer is correct to say that it follows an earlier paper we published and which we refer to in this technical note; however, the only similarity is in methodology. In our previous study we established a system by which we could create synthetic OC-Fe compounds with known OC and Fe concentrations, allowing us to determine the true recovery of Fe phases by chemical extractions. We used this system in the previous study to probe chemical interactions related to carboxyl content of organic matter. Here, we utilise this method to investigate the efficiency of the extraction methods. This manuscript contains entirely new data from a series of 4 experiments (time, dithionite concentration, sediment preparation methods for synthetic samples, and extraction of Arctic sediments). We believe this is presents original data and is sufficiently different from our previous work to warrant publication, and we felt the technical note format was most suited to the type of study we conducted.

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 pH, not the organic carbon that is extracted.

While we appreciate that the carrier phase of organic carbon (i.e., ferrihydrite) is dissolved in our experiments, the method we are testing was designed to release organic carbon bound to this carrier phase. We argue that the current title and study goal reflect this fact. In other words, we are not trying to quantitatively dissolve iron oxides, but we are testing possible iterations of a published method designed to quantitatively liberate iron-oxide associated organic carbon.

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.

We agree with the reviewer here, the method is aimed at extracting (as quantitatively as possible) the Fe-associated OC pool, not Fe itself - which also addresses the issue raised in the reviewer's previous comment. However, for a system where OC is quantified via the reductive release of Fe, all associated Fe must be reduced to fully liberate the OC pool. We show both in this study (Fig.1) and in Fisher et al. (2020) that full reductive release of OC is not achieved under our experiment conditions. The aim of our Technical Note is to provide colleagues who conduct this type of extraction with an awareness of possible factors (if any) that may affect the efficiency of their extractions. Additionally, given the wide variation in

applied methodologies we wanted to understand whether this was necessarily a problem for reproducibility, i.e. how robust the method is to certain (but admittedly not all the possible) variations in the protocol.

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 benefit of the method we deploy to investigate OC-Fe interactions is that the geochemical system is simplified as far as possible, as such we only consider ferrihydrite here. We realise that this approach also brings limitations, i.e. it does not consider goethite, hematite, magnetite etc. However, research progresses incrementally, and our study does not claim to give all the answers to all the questions in the OC-Fe realm. But regarding the issue of more crystalline iron oxide phases, we show that the tested method cannot fully extract OC and Fe in our ferrihydrite based system, so more crystalline phases are almost certainly going to be even more resistant to the chemical treatment. Indeed, Adhikari and Yang (2015) have already conducted these type of experiments in a hematitie based system (coprecipitated with humic acids) and show incomplete (<50% of Fe liberated) reduction of similar synthetic compounds. As the reviewer suggests, the experiments we conduct are therefore most applicable to modern sediments where ferrihydrite concentrations are high (e.g., near hydrothermal vents, in acid mine drainage deposits), however, this is also where current research suggests the largest fraction of the OC-Fe pool to reside. Recently it was also shown that goethite and hematite likely become less important in terms of OC association due to the desorption of OM during phase transformation (Jelavić, Mitchell and Sand (2020) *Geochem. Persp. Let)*.

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.

In the Fisher et al., (2020) paper a dithionite addition of 0.25g was used throughout, following Lalonde et al., (2012), so no investigation into the reductive capacity was made or can be determined from that study. The purpose here was to take account of the fact that many different iterations of this method have used different masses of dithionite to extract the OC-Fe pool, and a compilation of these is shown in Table 1. None of these studies, to the best of our knowledge, have quantified how much Fe can be extracted based on the varying amount of dithionite they use, but simply recommend a mass of sample which can obviously vary widely in Fe content, especially given the range of samples this method is applied to. We accept the reviewer's comment that we have not provided a definition for reductive capacity and have amended this in the abstract.

"We provide an assessment of the reducing capacity of Na dithionite in the CBD method *(the amount of Fe reduced by a fixed amount of dithionite)"*

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. 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.

The reviewer raises an important point here about the overall value of the study, and we are glad that in principle they agree that research in this area is important. We accept that some of the implications made in the introduction about our aim and the overall conclusions do not match up, particularly about whether the method should be improved/replaced by a new method. We wish to be clear that this is not a 'modified protocol' study; our aim here is not to replace that set out by Lalonde et al., 2012.

This has now been clarified by a restructure of the introduction with a new clear focus *"We aimed to establish whether widespread methodological variations in the CBD extraction protocol for OC-Fe$_R$ extraction influenced the efficiency, and therefore comparability, of this characteristic for marine sediment samples".* We have also modified the discussion to be less "superfluous" by concentrating around the newly outlined focus. We have added clarity in the introduction that this is not designed to be an all-encompassing study, and yes other studies have in isolation considered some of (not all) these factors for their influence in various extraction protocols but rarely do studies such as ours pull these variable parameters together or make it the focus of a discussion. We hope in creating this synthesis this results in a valuable technical paper for colleagues utilising the CBD method, increasing the awareness of pitfalls in reproducibility, particularly given that OC-Fe studies continue to evolve their methodologies.

The new scope of this study is formed on the basis that ,both historically and continually, a vast range of modifications have been made to the CBD method for OC-Fe and these are largely uncalibrated and difficult to compare to one another. Within this scope, rather than suggesting a replacement method, the discussion is now framed around understanding whether the variability in these pre-existing methods is a barrier to comparability and reproducibility between data sets. In other words, does it matter if different extraction times/ dithionite strengths/ sample preparation methods are used? We fully appreciate that we do not present all possible variations of all parameters, but clearly a few of the most critical ones.

We believe by narrowing the focus of the study we can retain its technical importance but avoid the apparent disappointment arising from comments regarding lack of completeness from reviewers who have, fairly, expected that this study is designed to replace or modify an existing method.

In addition, as pointed out in review 2 by Tom Jilbert, some of the topics we pick up on could be papers in their own right, e.g. freeze drying vs wet sediments for OC extraction, and we hope that this can lay the groundwork for future studies.

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 "OCFe"). Let's assume that it is %Fe.

Correct, %Fe is measured. Other reviewers raised a similar point and in response, we have added to section 2.6 of the methods to clarify that Fe was measured and how this is calculated.

"The recovery of Fe following the extractions was calculated by subtracting the control corrected loss of Fe from the initial sample Fe content. Maximal extraction of Fe is defined as the point from which further addition of Na dithionite does not further increase the extraction of Fe."

For example, the 20% OC-Fe sample contains 0.2x 0.25 g artificial sediment, or 0.05 g Fe.

In the 15 mL of reaction solution, this gives a. 0.06 mole/L Fe. The dithionite solution of 0.25 g $Na_2S_2O_4$ in 15 mL yields 0.093moles $S_2O_4^{2-}$ anion per L. Assuming that upon dispropotionation of the dithionite inwater yields two reducing equivalents, which is probably overestimated due to sidereactions with oxygen and other S decomposition products, we would have <0.18 mol/Ldithionite 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 worseor 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 failsmto 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%.

These details can be found in Table 2, where the terminology used has been simplified in response to previous reviewer comments – we apologise for the confusion that has led the reviewer to conduct these calculations however, they are incorrect. The 20% OC-Fe sample contains 0.2 g of artificial sediment and 0.05 g of the OC-Fe$_R$ coprecipitate. That is to say 0.05 g of the resultant complex from OC coprecipitation with ferrihydrite, not 0.05 g of pure Fe. We give the Fe value for this sediment sample as ~7 wt%, equivalent to 0.0175 g in a total mass of 0.25 g, which is less than a third of the amount assumed/calculated by the reviewer and very much in line with common Fe contents in natural sediments. Hopefully this removes some of the concern the reviewer had regarding samples at the 20% OC-Fe$_R$ content.

The reviewer is correct to say that the Fe contents become very high in the 50%+ OC-Fe samples (roughly equivalent to 17wt%+ of Fe), and it is for this reason we did not use these high Fe samples in the dithionite concentration experiments or time experiments. The 50-100% OC-Fe$_R$ samples are only used in the experiment to determine whether sample preparation methods affect Fe extraction from these samples. These were suitable samples to use for this experiment as this is an intracomparison of dried vs wet samples; the actual Fe extraction values are not of critical importance, but mainly the different between dried vs wet sample aliquots. Further, by performing an experiment on samples containing 100% OC-Fe$_R$ (i.e. only the coprecipitate) this serves as a control to ensure that interactions between the coprecipitate and the added sediment are not responsible for the differences observed here.

We are grateful that the reviewer has acknowledged that we explicitly give a comparison of the true Fe content of sediments in the paper. In response to a comment from Dr Jilbert we

have further reinforced this point by removing a reference to Fe clustering increasing sample Fe content. We have made an effort to be as transparent as possible in which samples relate to environmental content; however, the purpose, and benefit, of experimental studies such as this is to be able to create artificial conditions way beyond what is found in natural samples, providing a better understanding of fundamental chemical mechanisms.

Lastly, we would like to highlight that there are numerous instances where Fe contents of a sediment exceed the value for "normal" marine sediments, we have added detail of this in section 4.1 *"While reactive Fe content in bulk natural sediments is usually below 7 wt% Fe (e.g. Canfield, 1989;Raiswell and Canfield, 1998), spatial and temporal variation in Fe fluxes to the seafloor can result in Fe rich sediments e.g. near hydrothermal vents (Poulton and Canfield, 2006) or in Fe-Mn nodules (Hein et al., 1997)."*

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 experiment somewhat difficult to interpret.

We apologise for this omission. The samples were in fact vortexed following the addition of dithionite (and likewise for the controls), and this important detail has been added to the methods. Shaking throughout the extraction for this extraction protocol is impossible because the samples are incubated in a heated water bath. However, for the time experiments these were manually shaken every 15 minutes, as each sample was removed. We thank the reviewer for noticing this omission in the methods and have corrected accordingly. Reaction vial type was a centrifuge tube (see line 127).

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

This is discussed in line 153-157. Essentially, the synthetic OC-Fe$_R$ complexes are limited by production yields with a 5 L reaction volume producing only 5 g of precipitate. This was already scaled up from a usual 2 L reaction volume, but it is not logistically possible to conduct larger scale reactions, and recover the products, without industrial scale laboratory facilities. Therefore, careful choices were made over how this finite amount of sample should be used.

Firstly, behind every data point there are two samples given that a control extraction is conducted alongside each reduction. Secondly, as stated in the text *"Repeats of samples across the content gradient are in lieu of direct replicates for each unique sample condition."* Performing direct replicates from multiple precipitations is problematic as the actual amount of ferrihdyrite precipitated, and the amount of OC coprecipitated, varies between precipitations, i.e. you get a slightly different product each time you precipitate. So while the trends within each series of dilutions from the same precipitate are the same, averaging multiple different samples to represent one data point is likely to introduce an artificial error given we are not experimenting with absolute values. In the context of Figure 2, to maximise the data set, "replicates" occur at different dilutions of OC-Fe$_R$ (y axis) as opposed to individual point replicates. In this figure we see the same trend (= Fe recovery in wet extractions exceeds that of dry extraction) across all samples. In addition, the reviewer can be further assured by the inclusion of three different organic acid based precipitates, and the trend between wet and dry samples persists across three independent precipitations. Finally, while the experiment in Figure 2 is not designed to investigate the role of different organic

acids (due to inclusion of high Fe contents as noted by the reviewer), there is strong agreement in the overall trends between the results shown here and those in our previous study (which does investigate the effect of organic acids). This provides a good check and balance that the system here is performing as expected based on earlier experiments. We give an expanded explanation of the comparison between the two studies in an addition to section 4.2 following a previous reviewer's comment.

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.

Following our response to the reviewer's previous comment, where we suggested to refocus the scope of the manuscript, this will certainly shorten the introduction and discussion. However, both the other reviewers and this reviewer (see next comment) have asked for expansion in places to remove reliance on the Chem Geol paper which we agree is important and have been happy to fulfil (see response to Reviewer 1 and 2). In addition, we think that it is the purpose of a technical note in particular to report all technical aspects of the analysis in detail, to leave no doubt about the procedures.

The reviewer is mistaken to say section 2.7 is unnecessary, as organic C measurements are included in Fig.1 and directly discussed in the results; please see line 203-205 in the original manuscript. It is possible that the reviewer did not notice this was a commentary on the OC results as it is referred to as OC-Fe$_R$, (organic carbon bound to reactive iron). In response to reviewer 1 we have added a more explicit definition of this term at the start of the manuscript which we hope will remove any misunderstandings regarding terminology.

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.

This point was similarly made by reviewer 1 and 2, we have expanded the methods section relating to treatment of the carrier material to fully describe this.

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?

Yes, this links to the point made above, and we apologise for the confusing terminology. We have added a definition *"OC bound to reactive iron (OC-Fe$_R$)"* in the introduction following comments made by previous reviewers. We have also made a substantial effort to reduce terminology where possible, including a much wider use of wt% for dry masses and removal of unnecessary formulae such as Fe_2O_3.

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?

References to reactivity in this manuscript refer to the reactivity of Fe when reduced by dithionite, and this has been clarified for all in text mentions of reactivity. We have removed the first part of line 183 to make this sentence more concise.

"The contemporary CBD method of Lalonde et al. (2012) requires a 0.25 g addition per relative to 0.25 g of dried sediment sample. Here, the mass of dithionite added to our reaction was adjusted (0.125 g, 0.375 g, 0.500 g, 0.625 g) while the sediment mass remained at 0.25 g"

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.

Correct, this is a reference to OM extraction, supported by the statement on line 66 *"constraints associated with trying to qualitatively extract both OC and Fe."* We have added to the sentence to further reinforce this so it now reads *"Systematic improvement to the CBD method **for the extraction of OC-Fe$_R$** have not yet been attempted."*

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).

The method used in the study cited by the reviewer is a pH 4.8 dithionite extraction; we acknowledge the role of pH 4.8 extractions on lines 68-69 in the original study. However, these extractions are fundamentally different to the neutral pH OC-Fe extraction we conduct. In the Lalonde et al. (2012) iteration of the dithionite extraction (which we are working from), the neutral approach is said to reduce *"all solid reactive iron phases and the organic carbon associated with these phases"* (line 53). Therefore, while we agree with the reviewer that the outcome is not necessarily surprising, it is notable that other studies have come to other conclusions when applying this specific extraction to hematite samples.

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

See response to the first comment replied to in the "Further comments" section.

Line 54 "developed" knowledge?

Removed developed

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..)

We have checked and modified our use of content vs concentration throughout the manuscript in response to a similar point by reviewer 1. Gradient has been substituted for series.

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

Before mixing, clarified in the expanded methods section on carrier treatment. "This sample was freeze-dried then ashed (650 °C, 12 hrs) to remove OC, and fumigated with HCl vapour to remove inorganic carbon."

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

Lines 80 onwards discuss how other studies have varied methodological parameters; Lines 140 onwards discuss the specific changes we make in our method,

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

To clarify, the samples diluted 10 times (or not at all) were the supernatants from the seawater rinses which follow collection of the extraction supernatant. The highly concentrated samples from the extraction were strongly diluted as appropriate to fit the AAS calibration window. The seawater rinses have very low concentrations of Fe and hence do not need much (if any) dilution. We have clarified this in text.

"Dilutions of initial samples, in addition to the extraction supernatants, were conducted using MilliQ water, to produce a subsample within the calibrated concentration range of the AAS (1–10 ppm Fe)."

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.

For this purpose, they are the same thing, i.e., there is no control of accuracy with an international reference material. The machine is calibrated by sampling different masses of the manufacturer's standard. Then, during the sample run, this standard is resampled to check for drift. This is an important check in our method due to the use of decarbonated samples where drift can be a sign that the filter requires changing due to chloride accumulation. For analysing Fe concentrations by AAS at such high levels in experimental samples, the use of international reference materials is not common practise.

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.

The reviewer is correct here, but since we never reach 100% Fe extraction, this is not an issue in this application.

Line 224 Freeze-thawed samples? This experiment is not mentioned in the methods. Furthermore, this sentence (which is also discussion/interpretation) does not make sense. What "previous one". The sentence refers to Figure 1. There are no freezethaw or freeze-dry samples in Figure 1.

Please see Line 160-2 of the methods "Arctic Ocean seafloor sediment was collected (…), of which half was freeze thawed and half was freeze dried."

The sentence refers to the experiment between slurry and freeze-dried samples (shown in Fig. 2). We have added a clarification.

"This experiment only differed from that shown in Fig.2 by comparing freeze dried vs freeze thawed (not slurry) samples".

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.

The trend shown is a second order polynomial nonlinear fit. We address the issue of decreased Fe reduction as being a feature of Fe precipitation, an area of the manuscript we have expanded on in response to the review by Dr Henkel. The blue symbols represent maximal OC extraction rather than Fe, the OC/Fe ratio of <1 explains why they do not line up. A revised version of Figure 1 can be found in the response to Dr Henkel.

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.

We refer the reviewer to the improved Figure 2 created following constructive input from Dr Henkel which can be found in our reply. The issue of replicates has been replied to in detail earlier in this response.

Line 215 : "Typically"?

Removed

Line 251: Repetition.

Removed

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.

This section was removed in an earlier edit in response to comments from Dr Jilbert.

Line 284: Confounded?

Substituted with "reinforced"

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

Unclear what this comment refers to.

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.

Replaced *"released from the sediment"* with *"released from the coprecipitate complex".*

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

We have addressed this point in detail thanks to a suggestion from Dr Henkel about the potential of incorporating anoxic methods as an alternative to deal with Fe precipitation.

Line 399: There is no "standard" method against which to calibrate

This line no longer stands part of the revised manuscript following earlier edits.