

Interactive comment on “Fe(II) stability in seawater” by Mark J. Hopwood et al.

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GENERAL COMMENTS

This manuscript addresses a topic that is relevant to the scope of Biogeosciences. There is a clear rationale for the work, the experiments have been carefully designed and executed, and the data analysis and interpretation are reasonable. However, I felt that the scope of the paper needs to be more accurately represented and that some details relating to the experiments and data analysis were missing. Overall, I believe that this manuscript should be published after revision.

SPECIFIC COMMENTS

1. The title of the manuscript is too broad, to the extent that I find it misleading. The manuscript does not directly address the issue of Fe(II) stability in seawater – there

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are no measurements of thermodynamic constants (which the word “stability” implies), nor measurements or calculations of complex speciation, the underlying mechanisms are inferred or hypothesised rather than explicitly measured or tested, and the measurements are limited primarily to coastal seawater. This is all perfectly valid, but the manuscript really addresses iron redox speciation in coastal mesocosm experiments, and I would prefer to see a title more along these lines.

2. The assertions about “over-use of the “99%” statistic” (i.e. that “99% of DFe in the oceans is hypothesized to be present as Fe(III)-complexes” are subjective and I find this aspect of the Introduction to be overstated. It is true that “this observation explicitly or implicitly underpins the formulation of DFe in global marine biogeochemical models”, and that the influence of Fe redox speciation is often ignored. The authors also provide a nice summary of compelling evidence that Fe(II) is important in “two specific environments”. However, it does not automatically follow that the assumption that 99% of DFe is present as Fe(III)-complexes is invalid everywhere in the oceans, or that the “99% statistic” is “over-used”. To make this assertion objectively would require something like a meta-analysis of the literature to quantify the number of papers that make this claim, and the proportion of those that make this claim incorrectly. In my opinion, it would be better to just present the evidence and let the reader decide if they think this is an “over-used” statistic. I would suggest that the authors review the Introduction to remove or tone down subjective statements and ensure that any assertions are supported by an appropriate number of references.

3. In the Introduction there is a strong focus on why Fe(II) is important, but the background about what is known in relation to the abundance and behaviour of Fe(II) in the ocean seems incomplete. For example, the growing body of work (including by some of the co-authors of this manuscript) around the influence of organic exudates from marine phytoplankton on Fe(II) oxidation kinetics is not mentioned in the Introduction, but this would seem critical to understanding much of the manuscript and its rationale. In addition, while there is a brief overview of Fe(II) dynamics in the photic zone and in

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suboxic zones, it would also be useful to briefly review reports of Fe(II) measurements in other parts of the ocean.

4. Analysis of Fe(II) data was based on an assumption of pseudo-first order kinetics, but there are no details on whether this assumption was tested or verified.

5. I think it is highly problematic to exclude discussion of the Mesomed Fe(II) results from the manuscript because “Fe(II) concentrations were universally < 0.2 nM” (p. 3, lines 8-9). Given that you are arguing that Fe(II) is widespread and overlooked, excluding presentation of results from one set of mesocosms because Fe(II) was not measurable in those conditions could be perceived as cherry picking data. Again, I think this would be less of an issue if the scope of the manuscript as suggested by the title and Introduction was revised. If this is recast to make it clear that this is a study of Fe(II) dynamics in a discrete set of mesocosm experiments, then I think it is fine to mention the Mesomed experiments in this way without a detailed presentation of results. However, I think it is also important not to overlook these results in the discussion when generalising about Fe(II) behaviour.

6. The discussion about processes contributing to Fe(II) formation lacks mention of superoxide-mediated Fe reduction or other biological ferrireductase processes. This would seem remiss given that recent publications have suggested extracellular superoxide production may well be ubiquitous (e.g. Diaz et al., 2013, Widespread production of extracellular superoxide by heterotrophic bacteria, *Science* 340: 1223-1226) and is likely to influence Fe speciation (e.g. Rose, 2012, The influence of extracellular superoxide on iron redox chemistry and bioavailability to aquatic microorganisms, *Frontiers in Microbiology* 3:124).

7. The organisation of different aspects of the manuscript needs to be reviewed to ensure material is presented in the correct location. For example, the first paragraph of section 3.1 is discussion, not results. The second paragraph of section 3.1 is methods, not results. Details about measurement of hydrogen peroxide concentrations are not

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provided in the methods section at all, but rather addressed only by the statement “as per Hopwood, 2018” in the results section.

8. P. 1, line 14. I suggest changing “exclusively” to “almost exclusively” or “primarily”. It is not strictly correct to say that dissolved Fe speciation is assumed to consist exclusively of Fe(III)-L, as Fe^v is generally also considered (although minor).

9. P. 2, lines 31-32. The argument that “the potentially widespread presence of Fe(II)” implies that “redox cycling is an important feature of marine Fe biogeochemistry” is a circular argument. The three cited papers do not show that Fe(II) is potentially widespread – they show that Fe(II) is persistent in certain specific environments and locations studied in this papers. I don’t mean to be overly critical about this – I think Fe(II) is important and possibly overlooked – but I think it’s important to be objective and precise.

10. P. 17, lines 9-11 and 19-21. This hypothesis is not plausible, in my opinion. A difference in rate constants between different Fe(II) concentrations could be related to a difference in chemical mechanism, but should be completely independent of calibration. Also, there are several studies of Fe(II) oxidation kinetics in seawater that have been conducted at low nanomolar concentrations such that there is a coherent mechanistic understanding (and ability to predict) Fe(II) rate constants from the low nanomolar range right through to the micromolar range.

TECHNICAL CORRECTIONS

11. P. 1, line 20. I suggest changing “retarded relative to” to “less than”. Rates can be fast or slow, but rate constants are large or small.

12. P. 1, line 25. Please add a qualification to this sentence explaining under what conditions your work challenges these assumptions (e.g. in coastal surface waters?).

13. P. 2, line 8. Ligands are not necessarily small or organic. Perhaps could change this to “Organic ligands (L) capable of complexing Fe(III) can. . .”.

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14. P. 2, lines 24-26. This sentence seems like it belongs in the next paragraph. . . I can't see how this relates to the presence of Fe(II) in suboxic or photic zones.
15. P. 2, line 28. "There is a paucity of Fe(II) data. . ." – what sort of Fe(II) data?
16. P. 2, line 29. What do you mean by "kinetic availability"? Do you mean kinetic lability?
17. P. 2, lines 34-35. "as evidenced by over-use of the 99% statistic" – what evidence? No citations are provided and this is not tested robustly, as stated in point 2 above.
18. P. 3, lines 6-10. Following on from point 5 above, I find it confusing that some Mesomed results are included in the results, but no details are provided in the methods about these experiments, other than these couple of sentences. I think you need to treat this dataset in a similar way to the other mesocosm results, namely describe the method details in full, and fully account for the Mesomed results in your discussion.
19. Tables 1A and 1B. It would make more sense to me to label these Table 1 and Table 2, as they show quite separate information. Furthermore, it would be useful to provide coordinates for the mesocosm locations in Table 1.
20. P. 6, line 4. Can you provide any information about the spectral quality of the lighting?
21. P. 6, line 25. Should this be "trace metal clean low density polyethylene" rather than "trace metal low density polyethylene"?
22. P. 7, line 22. Change "as described by (Paulino et al., 2013)" to "as described by Paulino et al. (2013)".
23. P. 9, equation 1. Please define precisely the meaning of Vaddition and Vmesocosm.
24. P. 11, lines 6-7. The sentence "Before presenting. . ." is redundant and could be removed – this is self-evident to the reader.

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25. P. 11, lines 10-11. Where the correlations statistically significant?
26. P. 12. Please define the meaning of the error bars on Figure 3.
27. P. 13, line 1. Does "highest resolution" refer to temporal resolution? Please clarify.
28. P. 13, lines 14-16. Is linear regression meaningful for these data? Why use linear regression in this case?
29. P. 14, lines 2-5. What do the +/- symbols represent here?
30. P. 14, line 4. Change "measurements was" to "measurements were".
31. P. 14, line 21. There is no section 3.3.
32. P. 15. Figure 5 is unreadable as it is too small.
33. P. 15, line 11. Should this refer to Fig. 5(c) rather than Fig. 5(b)?

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