

Interactive comment on “Ocean acidification affects iron speciation in seawater” by E. Breitbarth et al.

Anonymous Referee #2

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GENERAL COMMENTS

The strength of this paper is that the authors have addressed a very relevant scientific question (i.e. what effect will ocean acidification have on iron biogeochemistry in the future?) and present interesting novel data. The general conclusions are also interesting and are, for the most part, supported by the data presented along with the recent work of others.

There are some major issues that I have noted. The main weaknesses lies in (i) the initial experimental design (no controls for Fe(II) oxidation rates, no initial Fe concentrations and lack of trace metal protocol described) (ii) a lack of detail given in the methods section (i.e. needs to be at the level of detail where another worker to be able to repeat these kinds of experiments in the future) and (iii) a slightly confusing results

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and discussion section which at present may confuse readers who are not very familiar with Fe biogeochemistry. It is my recommendation that both (ii) and (iii) be revisited. The lack of clarity in the results and discussion is partly to do with just wording in the sentences (which is fixable and I have made some recommendations on this) but there are also some leaps of faith in the logic which need consideration.

In terms of the validity of the work, despite what appear to be iron saturated conditions, the dFe story seems to be valid as the trends of the mean results of each treatment were different according to the standard deviations. For Fe(II) there are also definite trends in the rates identified which also relate to the different conditions in the mesocosms. I am not convinced that “the influence of phytoplankton bloom derivatives on the actual half-life times are obvious”. To really know this there would need to be some kind of control with no phytoplankton present (?) There are some really interesting questions that can be raised on this whole matter. The first question is how repeatable are the rates given by Millero and co-workers with different seawaters and different experimental setups? Maybe this question has to be addressed first before we start using these calculations as justification for the effects of ligands and exudates?

The other question raised is whether chelating ligands or exudates really have an effect on oxidation rates at these timescales. Using kinetic models can (what are presumably nanomolar concentrations of) Fe(II) binding ligands within exudates, actually bind to the nanomolar concentrations of initially inorganic Fe(II) in the several minutes of oxidation? (I think there is some discussion of this the papers by Rose and Waite?). Also can we ignore the possibility of other redox active species in the bulk phase, such as back reactions with reactive oxygen species, which are produced at considerable rates under coastal bloom conditions? Any further interrogation of the data to answer these two questions would really benefit the paper and also be really interesting.

Finally, hydrogen peroxide was not measured which means a major assumption has to be made that the peroxide concentrations were consistent between mesocosms and points in time. Nevertheless the trends in rates observed seem to be consistent rather

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than random but any further discussion or calculations on the potential effect of this oversight could further strengthen the conclusions made.

SPECIFIC COMMENTS

Title: I suggest (although I understand this will be at the authors and editors discretion!) that the title of this paper be more specific e.g. 'Ocean acidification affects iron speciation in coastal mesocosms'.

Introduction: generally this read well, there are some recommendations below Page 6782 I suggest moving sentences 18-22 to the end of the intro. For clarity and to avoid repetition. The authors could add Millero and coworkers Fe solubility papers -Marine Chemistry 77 (2002) 43– 54 (Page 6782 line 25).

Line 25-26 logic does not follow, perhaps remove "In addition to. . .coastal seawater"

Page 6783 Line 10 This could imply that it only occurs in temperate waters perhaps you could say warm waters or tropical and temperate? Line 15 There are also a few papers showing the significance of Fe(II) in shelf waters (e.g. Croot and Hunter, Marine Chemistry 1998, vol. 62, no3-4, pp. 185-201 and Ussher et al. Limnology and Oceanography 2007, vol. 52, no6, pp. 2530-2539) Line 21-23 I don't think the statement that photo-reduction is the main pathway of Fe(II) production is absolutely certain for all waters and a reader could interpret this as there being no need to consider any other sources. It is certainly the most characterized but there remain other less well quantified sources (e.g; biological cycling, sediment sources in shelf waters and reduction in sub/anoxic waters). Some additional words and references could be added on this for readers less familiar with the literature.

Methods: This section needs more detail. Although details may be given in the Schultz paper, detail specific to trace metal sampling and handling is necessary here. Also some more detail on the analytical procedures followed would be really helpful. This can easily be addressed by following the level of detail given in methods sections in

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previous published work by some of the authors. I think another 2 or 3 paragraphs are needed here.

For example: how were the mesocosms cleaned and purged, how and where was the sampling and processing done. What were the final concentrations of inorganic N and P added? did you use filtered air? which filters and sample bottles were used, how were they cleaned? How was the sub-sampling done cleanly? How was the Fe(II) analyser set up in situ? 12V power supply? Where did you source your Fe(II) and Fe(III) standards? Did you check that the (presumably) acidic Fe(II) standard spiked into the seawater for oxidation experiments did not alter the pH? How did you calibrate for Fe(II) measurements? Were there any possible interferences on the Fe(II) method (e.g. Co(II), V(IV), Mn(II))?

I am particularly interested in how the Fe(II) oxidation rates were obtained experimentally/practically, was there any mixing used? How repeatable were the data? How was the CO₂ partial pressure maintained during and after removal from the mesocosm? e.t.c.

Page 6784 Line 23 is tFe unfiltered? If so, could this be stated. Presumably the Waterville reference is for the analyzer used whereas the Bowie reference is for the method used. Could this be made clear please.

Page 6785 Lines 11-15 What were the oxygen concentrations used here?

Results and discussion: Overall the discussion and conclusion about the observed increase in dFe concentrations in future surface seawater is supported by evidence from previous studies of Fe seawater chemistry at varying pH by other workers and is evidenced by the data presented here. In hind sight, more data would have really strengthened this (i.e. more controls, initial dFe concentrations and >15 data points-admittedly they are triplicates!). Other comments on this have already been presented by reviewer 1.

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Page 6786 Line 1 Uptake: As large quantities of new cells were being produced and mesocosms were used, should cell surface and wall adsorption be ruled out here? Line 5 Again this could just as equally be desorption as well as mineralization(?) Line 5 Is there is any proof that these particles were 'relatively unreactive'? Line 16 Can the authors give an indication or values of what these solubilities might be?

Page 6787 Line 6 How could a diel cycle be observed using the sampling frequency shown? Presumably there were other data gathered? Line 18-23 This sentence really needs reconsideration. If it is to be used perhaps an equation or some illustrative values could be shown. Line 23-25 I disagree with the statement that the contribution of peroxide will only have implications above 200 nM. Can the authors convince the reader (and this reviewer) of this with some numbers (e.g. using the peroxide oxidation kinetics from Millero)? Perhaps this could even be indicated in the half lives of Figure 6.

Page 6788 Line 3-5 I am not convinced that the different rates to predicted values can be solely be attributed to exudates, as is implied. Can the authors either suggest other mechanisms or supply more proof (e.g. a control; free of phytoplankton)? (Also see general comments) Line 15-16 The sentence starting 'Effects thereof . . .' is not really needed. Lines 20-23 I do not think this can be stated with such certainty and I don't really follow the logic. Any statement on residence time is always difficult to evaluate. For example if the bioavailable dFe pool in surface waters is increased and constantly replaced due to partitioning but the rate of downward flux of Fe incorporated in cells is greater than the physicochemical loss dFe. This could actually reduce the residence time of Fe? I think it would also depend on the original source and speciation of the Fe considered e.g. aerosol Fe versus Fe chelates and organic colloids. Can the authors shed more light on this with some references to models or flux estimates or alternatively or could this sentence be reworded to 'may' or 'could'?(!)

TECHNICAL CORRECTIONS

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Author affiliations should appear in order as they appear

Page 6782

Line 18 Capitalize first letters in title of study (?) Line 23 Give a range or indicate what is "low iron" solubility

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Line 5 remove "return" Line 8 replace "the" with "a" substrate Line 10 remove comma before "but" Line 24 remove 'for' and replace with 'Based on estimates of' Line 26 remove 'until' and replace with 'by'

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Line 2 remove 'particularly evaluated' replace with 'determined' Fe(II) concentrations not 'levels' Line 21 Avoid the use of 'Please see' throughout. Perhaps 'More detail can be found . . .' would be better. Line 24 Insert 'sub-sampling' before 'was focused'

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Line 3 Replace form with 'from' Line 9 The first letter of Naperian should be capitalized Line 10 Full stop needed here. Fe(II) standard additions vs. what? Line 25 dFe is abbreviated earlier in manuscript

Page 6786 There are several instances throughout the R and D here where the past tense should be used for things that were completed or observed. E.g. Line 16 should say 'resulted' in. Please check this throughout R and D.

Line 3 Replace 'Distinctions in' with 'Distinct differences between' Line 7 tFe is abbreviated earlier in manuscript Line 16 remove 'Any' and replace with 'The predicted' Line 26 use past tense i.e. 'were' Line 25-29 Sentence is too long and needs clarifying

Page 6787 some paragraphs are desperately needed on this page. Could the term

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'future ocean scenarios' used throughout to refer to the mesocosms be replaced by something more specific like 'CO₂ treated mesocosms' Also could all 'Half-lives' be changed to 'half-lives'

Line 1 Replace 'The' with 'A' Line 5 Remove 'Fast moving' and replace with 'though' Line 7 remove 'While' Line 8 A new sentence is required after the references Line 11 Fe²⁺ 'aqua ion'? Line 12 insert 'the oxidation of' Fe(OH)₂ Line 13 past tense needed 'caused' Line 16 what is meant by 'especially'? Line 17 Replace 'aid in' with 'increase'

Tables: FE needs to be replaced with Fe and the days corrected on Table 2. Also correct "after incubation (ing?) the mesocosms". Can you briefly explain the SD given in the title? Anything 'logged' should not have units.

Figures: The symbols should be labeled 'dots' or 'circles' instead. These presumably were mean values of the triplicate experiments? Could this be stated in the title. Also could anything that was calculated rather than measured be stated as calculated. Figure 6. remove bracket around Millero et al in title. Presumably these are calculated based on the temperatures and oxygen concentrations shown in the other figures, if so could this be made clear in the title as well as the meaning of the different shades/colours.

END OF REVIEW

Interactive comment on Biogeosciences Discuss., 6, 6781, 2009.