

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

Anonymous Referee #1

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This paper presents an interesting data set in which Fe biogeochemical parameters were followed during a three week CO₂-enriched mesocosm experiment. Despite some recent speculation about possible effects of ocean acidification on dissolved Fe speciation, hard data on this subject is still missing from the literature. For this reason, these results will be of interest to many chemical and biological oceanographers, and the subject of the paper is certainly very appropriate for this special issue of BG.

General comments

The paper unfortunately has two major experimental design shortcomings that compromise the interpretation of the results. The first and most serious is that the mesocosms were clearly quite affected by Fe contamination. Fig. 4 shows that total Fe concentrations were perhaps 4 to 20 times higher in the mesocosms than in the surrounding

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fjord water, and maybe $\frac{3}{4}$ of the dissolved Fe measurements were as much as 3 times higher than in the fjord water as well. The scattered nature of the data shown in Fig. 4 are characteristic of accidental contamination, which typically shows a great deal of random variability. To their credit the authors do show these data and do admit briefly (page 6786) that there must have been “an input of relatively unreactive particulate Fe during the filling process”. There is no description at all in the methods of any attempts to use trace metal clean techniques during setup or sampling of the experiments, for instance were the bags themselves and the sampling equipment at least acid-washed? More explanation is needed here- what could be the source of these very high levels of particulate Fe, were the mesocosms filled using steel piping and water pumps, were steel frames used in their construction, were the bubbling and mixing systems a potential contamination source, and so forth?

The answers to these questions have a great deal of bearing on the interpretation of their results. Could the large dissolved iron increases in the higher CO₂ treatments be due to pH effects on dissolution of contaminating elemental Fe or Fe oxide particles, rather than being from some biologically-derived process? I don't think that the statement quoted above that this particulate iron was “unreactive” is really supported by any data. Or could these increases be partly due to additional contamination occurring over the course of the experiment- presumably there were a lot of other researchers sampling the mesocosms on a daily basis by immersing sampling equipment of unknown cleanliness. This whole contamination issue is really unfortunate, but doesn't have to prevent publication as long as it is explicitly acknowledged and the implications for the results carefully considered in the discussion. Right now, this is not the case.

The other big flaw in the data set is the lack of measurements of any kind for the first week or so of the experiment. Of course, to properly interpret the changes in Fe speciation they see during the last 2 weeks, this initial data is needed. It would also help to evaluate the source and seriousness of the Fe contamination problems discussed above. Obviously they can't go back and redo this, but it was a bad decision

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for whatever reason to not start sampling until the experiment was well underway.

Despite these serious problems, their data set on increasing total dissolved Fe and Fe(II) concentrations with higher CO₂ levels is interesting and worth publishing. Even if the source of most of the iron they measured is from contamination (which seems probable), there still must have been more biological ligand production in the higher CO₂ treatments to maintain such high total dissolved levels and slow down Fe(II) oxidation rates below predicted values. These are significant results. Some thoughtful consideration and additional discussion of the two major problems I raised above is badly needed to meaningfully interpret all of their results, though.

Specific comments

The methods section on page 6785 says that Fe(II) oxidation rates were only measured at the end (day 25) of the experiment. Again this is too bad, a time course would have been very interesting. I am confused though about what the Fe(II) oxidation rates are that are presented in Table 2, they appear to be labeled as being from days 20 and 22. If so, why not combine Table 2 with Table 1 and present all of the Fe(II) oxidation results in the same place? And what does "in synchronization with carbonate system measurements on day 11 and day 13" in the legend to this table mean? Were Fe(II) oxidation rates compared on days 20 and 22, but using pH values from days 11 and 13? If so, this is hardly ideal, but the wording is confusing enough that I'm not sure exactly what was done here.

Fig 6.- This figure shows calculated Fe(II) half-lives, not actual measured results. This is clear from the figure legend but less so in the results text. Also, it might help readers to add in shading on this figure showing the ranges of pH experienced in the three experimental treatments.

Page 6786, top- This statement about remineralization during bloom decline is an example of one that needs to be qualified in light of the contamination problems. This increase in dissolved Fe late in the experiment could just as easily have been due to

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cumulative contamination from repeated sampling.

Page 6786- Using an average diatom Fe-replete Fe:C ratio of 65 from Sarthou et al to calculate bloom iron demand in the absence of initial measurements involves major uncertainties- for instance, actual Fe:C ratios could vary by nearly an order of magnitude either direction. This is also an example of a place where the lack of initial Fe measurements really hurts the paper.

Page 6786, last paragraph- I believe the first demonstration of increased Fe complexation during an in situ Fe addition experiment was published by Rue and Bruland (1997, L&O 42 p 901) from the IronExII experiment. It would be appropriate to reference this paper here. Page 6787- This is the first mention of the significant temperature increase during the experiment, which of course could potentially greatly affect kinetics of both chemical and biological rates. A somewhat better description of important trends like this in the experiment is needed in the methods, for those readers who haven't read the Schulz et al paper.

In spite of the problems with contamination and sampling design, the paper definitely has an important message about changing Fe speciation under high CO₂ conditions. If the discussion is appropriately altered to carefully consider what the study can (and can't) teach us despite the methodological and experimental design shortcomings, it will make a good addition to the literature on ocean acidification and iron biogeochemistry.

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

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