Review of Biogeosciences Discussions, 6, 6781-6802, 2009: "Ocean acidification affects iron speciation in seawater" by Breitbarth et al.

This paper presents a novel data set that examines the influence of elevated CO_2 concentrations and resulting low pH on iron solubility and iron speciation during a phytoplankton bloom in a coastal mesocosm study. The measurements clearly show that a tripling of pCO_2 from 350 microatmospheres (μatm) to 1050 μatm caused up to a two-fold increase in the concentration "dissolved" iron, operationally defined as that passing through a 0.2 μm-pore membrane filter. The authors suggested that the increased "dissolved" iron was related to the biological production of iron-binding organic ligands by phytoplankton or to the production of filterable ferric iron colloids. However, an enhanced ferric chelate production in the high CO_2 mesocosm seems unlikely as the algal growth in this enclosure was only 10% higher than that in the low-CO_2 mesocosm, as indicated by particulate organic carbon measurements. Much more likely is the production of small colloids at high CO_2/low pH. Their production would be enhanced by elevated photoredox cycling, which would continuously produce soluble monomeric iron hydrolysis species (Fe(III)') that would polymerize into small iron hydroxide colloids. Another possible explanation is an increase in iron hydroxide solubility that would occur if the pH dependence of organic chelation of iron is less than that for ferric hydroxide precipitation. This pH dependence occurs because all organic chelators that bind iron are weak acids, and thus, iron chelation almost always is accompanied by the release of bound hydrogen ions from the ligand:

$$Fe^{3+} + H_nL = FeL + nH^+$$

In the above reaction, n is the number of hydrogen ions released during the iron chelation (for simplicity all charges are not included). If $n < 3$, then chelation will increase with decreasing pH relative to the competing reaction of iron hydroxide precipitation:

$$Fe^{3+} + 3H_2O = FeOH_3(solid) + 3H^+$$

However if $n>3$, then iron hydroxide formation will be favored at lower pH over the competing chelation reaction. At present the pH dependence of ferric chelation to natural organic ligands is not known, so it is uncertain what effect elevated CO_2/low pH will have on iron solubility in the presence of these ligands.

The authors also found up to three-fold higher midday Fe(II) concentrations in the mesocosm with the highest pCO_2 and lowest pH relative to concentrations at the lowest pCO_2. They attributed the presence of thermodynamically unstable Fe(II) to the photolysis of ferric chelates, in which the bound iron is reduced to Fe(II) and the ligand is oxidized. The released Fe(II) is then rexoxidized back to Fe(III)' by reaction with molecular oxygen and other oxidants (e.g. hydrogen peroxide). The authors attributed the increased Fe(II) concentrations to an increased rate of photolysis of organic ferric chelates, resulting from a decreased stability of these chelates with decreasing pH. This may well be occurring, but the increased concentration of Fe(II) at lower pH in the high CO_2 treatment may be more directly related to the lower rate of reoxidation of photoproduced Fe(II) back to Fe(III). Since the residence time for Fe(II) is short (on the order of minutes) Fe(II) concentrations can be considered to be at steady state, with Fe(II) concentration proportional to the ratio of their photochemical production rate and their chemical reoxidation rate (Sunda 2000). Thus, if there is no change in the concentration of photolabile ferric chelates or sunlight, a two-fold decrease in the specific Fe(II) oxidation rate (i.e., the oxidation rate constant) will result in a twofold increase in the steady state concentration of Fe(II). This is indeed what is observed. In their measurements on days 11 and 13, the authors observed an ~2 fold decrease in the measured Fe(II) oxidation rate constants between the lowest and highest pCO_2 mesocosms on days 11 and 13, which was enough to account for most of the two- to threefold higher midday Fe(II) concentrations. As the authors noted, the measured rate constants were lower than those predicted from the published rate constant data for the oxidation of Fe(II) by molecular oxygen determined as a function of pH (Millero et al. 1987). Such a discrepancy has been observed previously in coastal seawater (Miller et al 1995), but the reasons for this are unknown. The authors suggested that the lower rate constants in the natural seawater could be due to chelation of Fe(II) by some unknown organic ligand, a plausible explanation that has been suggested previously (Miller et al. 1995).

I agree with the authors that ocean acidification from higher ocean CO_2 concentrations could increase the biological availability of iron to phytoplankton due to increased concentrations of bioavailable iron species (Fe(II) and "dissolved" iron). Furthermore, I agree that any resultant increased biological uptake of iron could increase algal productivity in the roughly 30-40% of the ocean where iron limitation restricts primary productivity. However, I think the effect is more likely to be a direct effect of changes in iron speciation, rather than an indirect effect as suggested by the authors. They suggest that increased iron bioavailability would result in "increased residence times for Fe in surface seawater leading ultimately to an enhancement of iron bioavailability since equilibrium partitioning eventually restores the bioavailable Fe pools that have been depleted by biological uptake." I don't understand the reasoning here, as increased iron bioavailability and resulting enhanced biological uptake should cause a depletion of iron concentrations in near-surface seawater and thus lead to shorter, not longer, residence times. I do agree with the authors that the increase in algal photosynthetic fixation of carbon resulting from higher iron uptake rates could increase the ocean's biological CO_2 pump and thereby draw down atmospheric CO_2, providing a potentially important negative feedback on ocean acidification and global climate change. And I agree that such potential feedback mechanisms involving iron speciation clearly warrant further research.

Specific comments:

Page 6786, lines 16-20. This statement may not be true. First, the change in iron solubility likely reflects the relative pH dependence of iron chelation and iron hydroxide precipitation reactions, as discussed above. Thus, the increase in filterable iron concentrations does not necessarily suggest an increase in ligand production or an increase in the formation of filterable iron hydroxide colloids.

Page 6787, lines 5&6 – The patterns observed – highest Fe(II) near midday, with decreasing concentrations later in the day – is consistent with daytime changes in solar radiation intensity and concomitant changes in photo-production of Fe(II). In diel studies, Fe(II) concentrations often peak before the daily peak in irradiance because of a progressive increase in concentrations of photochemically produced hydrogen peroxide and increasing pH and O_2 concentrations from photosynthesis during the light period, which can increase specific rates of oxidative removal of Fe(II) as the day progresses.

Page 6787, lines 6-9 – This is a poorly worded sentence whose meaning is not entirely clear. The higher Fe(II) levels at high CO_2/low pH does not necessarily indicate "a higher photolability of iron chelates at low pH." The higher Fe(II) instead may be largely related to low rates of oxidation and removal of Fe(II).

Page 6787, lines 11-13 – This statement is untrue. According to equilibrium calculations of Byrne et al. (1988) the majority of ferrous iron is present as the free aquo ion in the pH range 7.6 to 8.2 in seawater, and < 2% occurs as iron hydroxy complexes.

Page 6788, lines 4&5 – This statement is a bit strong given the uncertainties. It is not at all "obvious" that the lower specific Fe(II) oxidation rates in the bloom water is due to the retarding influence of organic phytoplankton bloom derivatives.

Page 6788, line 10 – Ditto here. The lower than expected Fe(II) oxidation rates, especially at low pH, may indeed be the result of complexation of Fe(II) by some unknown organic ligands, but there is little hard evidence for this. The arguments here need to be softened.

Page 6788, lines 17-19 – This statement is not entirely supported by the data. The authors present no hard evidence for pH induced changes in organic complexation.

Page 6788, lines 20-23 – The reasoning here is unclear and appears to be shaky. It's not at all clear how an increase in the biological availability of iron will increase iron residence times, and thereby further increase iron bioavailability. Increased iron bioavailability should increase biological uptake and removal of iron via vertical settling of plankton and detrital particles, which should decrease iron residence times. However, the increased biological iron uptake should increase photosynthetic fixation carbon and carbon export to deeper waters in iron limited regions of the ocean.

Technical comments and corrections:

Page 6782, line 7 – Change wording to "..in response to CO_2 enrichment **and concomitant lower of pH**, suggesting….". It is the lowering of pH, not the elevated CO_2, that is the driving factor.

Introduction – Much the introduction is poorly organized and portions are poorly written. There needs to be much more said on the topic of the well-documented effect of pH on iron speciation and redox cycling. This includes effects on the solubility of iron oxides, the stability of iron chelates, and the rates of reduction (and photoreduction) of ferric chelates to Fe(II) and reoxidation of released Fe(II) to Fe(III). These well documented pH effects provide the rationale for the study.

Page 6782 – Change wording to "…photochemical **redox** processes…".

Page 6782, line 25 to page 6783, line 2 – The meaning here is unclear.

Page 6783, lines 5&6 – This sentence is unclear as written.

Page 6783, lines 9&10 – “in temperate waters” What about subtropical and tropical waters where oxidation rates should be even higher? I suggest changing the wording to “…in temperate **and tropical** waters **results** in limited concentrations **of Fe(II)**. Half life times **of Fe(II)** range…”

Page 6783, line 26 – Should be “..units **by** 2300…”.

Page 6784, line 1 – Should be “different **partial pressures of** $\mathbf{CO_2}$.” “pCO_2 concentrations” is incorrect terminology.

Page 6784, line 2 – Change wording to “We **measured** dissolved..”.

Page 6784, line 3 – Change wording to “mesocosm study **to determine** if…..”.

Page 6785, line 3 – Typo. Change to “..samples **from** day…”

Page 6785, line 3 – Change wording to “…**resulted** in pH **values of** 7.67-7.97,…”.

Page 6786, line 15 – Change wording to “…approximates the **changes in** iron **concentrations** detected in the Fjord water during the bloom.”

Page 6786, lines 25-30 – The meaning of this sentence is unclear.

Page 6787 and Tables 1&2 – Presenting Fe(II) oxidation rate constants in log units is very confusing and is unnecessary given the values of the constants. The straight constants should be presented.

William Sunda

References:

Byrne, R. H., Kump, L. R., and Cantrell, K. J.: The influence of temperature and pH on trace metal speciation in seawater, Mar. Chem., 25, 163-181, 1988.

Miller, W. L., King, D. W., Lin, J., and Kester, D. R.: Photochemical redox cycling of iron in coastal seawater, Mar. Chem., 50, 63-77.

Millero, F. J., Sotolongo, S., and Izaguirre, M.: The oxidation kinetics of Fe(II) in seawater, Geochim. Cosmochim. Ac., 51, 793–801, 1987.

Sunda, W. G.: Bioavailability and bioaccumulation of iron in the sea, In: Turner, D. R. and Hunter, K. A. [eds], The Biogeochemistry of Iron in Seawater, Wiley, New York, pp. 41-84, 2001.