# Workshop Highlights Role of Iron Dynamics in the Carbon Cycle

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The role of iron in regulating rates of carbon cycling and the accumulation of particulate organic carbon standing stocks has become increasingly apparent in the past 15 years. Incorporation of iron dynamics in biogeochemical models has dramatically improved our ability to simulate ecosystem processes in the oligotrophic regions of the world ocean. Basin to global scale models can now reproduce the observed dissolved iron and macronutrient distributions of the High Nutrient and Low Chlorophyll regions with reasonable levels of phytoplankton biomass and primary production. However, there are still a number of large uncertainties in our understanding of iron chemistry and biology that are hampering our ability to prognostically model ocean biogeochemical cycling and the marine ecosystem response to climate change. A US JGOFS Workshop on Iron Dynamics in the Carbon Cycle was held at the Monterey Bay Aquarium Research Institute in Moss Landing, California from June 17 to 19, 2002 to address these issues. A complete report of the meeting is available on the US JGOFS Synthesis and Modeling Web Page (http://usjgofs.whoi.edu/mzweb/iron/iron\_rpt.html). Here, we report some of the major highlights and recommendations.

#### Iron Distributions

Perhaps the most pressing need from a large scale modeling perspective is for a global database of dissolved iron distributions in the oceans similar to those available for inorganic carbon and macronutrients. Such an iron database has not been accumulated because of the difficulties in measuring exceedingly low levels of iron (surface concentrations <0.1 nM and ocean mean concentration ~0.7 nM). Significant progress has been made in developing techniques to make large numbers of iron measurements in seawater. While discrepancies remain between methods, the errors are on the order of several tenths of a nmol/L Fe. It was concluded that, with modest additional efforts at intercalibration, it would be feasible to begin large scale efforts to map global distributions of iron and other biogeochemically significant trace elements.

## External Iron Inputs

The deposition of mineral dust in the oceans is a key source of iron that modulates biogeochemical processes. Attempts to model this transport and deposition of mineral dust are increasing in complexity and accuracy, but observations are lacking. Modeled deposition rates in remote regions can disagree by a factor of 10 or more. More direct measurements of aerosol concentration and deposition are required. There are significant efforts to develop autonomous, moored instruments to measure both of these quantities. Such efforts should be encouraged.

Solubility of iron in aerosols remains a large uncertainty. Results from laboratory studies span a range of at least an order of magnitude, with recent estimates of the amount of soluble iron within mineral dust of 1-3 %, which is well below the earlier estimates of ~50%. Recent field observations indicate that even larger values (>50%) may be observed in natural systems.

Continental margins are also a large source of iron. Much of the iron is derived from sedimentary sources. Because the iron source need not be directly coupled to macronutrients in the source water, iron limitation may occur in the coastal zone. Presentations at the workshop demonstrated that coastal iron limitation can play a major role in regulating coastal ocean ecosystem rates, biomass and structure. The coastal ocean accounts for 20% of ocean primary productivity, and perhaps 50% of the carbon export and 90% of carbon burial. Iron limitation of coastal primary production may be particularly important at low stands of sea-level during the glacial maxima. Iron inputs to the ocean interior from continental margin sources are not yet included in any of the global iron models.

Iron Regulation of Ecosystem Processes

Just one decade ago, there were intense debates about the role of iron in controlling biogeochemical processes. Since that time six open ocean iron fertilization experiments have been conducted (Table 1). All have shown enhanced rates of primary production and biomass accumulation following iron addition. Iron enrichment experiments conducted in bottles during the US JGOFS programs have shown a remarkable commonality in the level of iron that stimulates a community response. Community growth rates have a half-saturation constant of approximately 0.1 nM Fe, when fitted with a Michaelis-Menton model, in nearly all pelagic environments. Such parameterizations have formed the basis for incorporation of iron into global ecosystem models.

Most models assume that iron is recycled in a similar manner and at similar rates to the macronutrients. However, iron may behave differently than the major macronutrients within phytoplankton cells and within ecosystems. Observations made over the last decade suggest that Fe/C ratios are much more variable than N/C or N/P ratios in plankton and the water. Detailed measurements of key elemental ratios (Fe/C/N/P/Si/CaCO3) using clean techniques could answer many of our remaining questions about iron and carbon cycling in the oceans.

Many discussions at the workshop focused on iron speciation and the role of ligands in regulating bioavailability and biogeochemical cycling in the oceans. It is now known that >99% of the dissolved iron in the upper ocean is strongly complexed by organic molecules. The organic ligands are distributed more or less uniformly in the oceans, but there have been very few measurements. Currently, ligands that bind iron are only crudely included in models. Many marine micro-organisms are capable of producing iron binding ligands, but the sources and sinks, lifetimes, and turnover rates between ligand pools and the processes which govern these transformations (biology vs. photochemistry) are simply unknown.

The bioavailability of various iron sources (dissolved and particulate) is also poorly known. Phytoplankton and bacteria have a complex array of Fe acquisition systems (e.g., siderophore mediated uptake, reductases, ligand production, and phagotrophy). Processes such as photochemistry clearly cause redox cycling of iron between different chemical species, thereby modifying bioavailability. There also appears to be some degree of species specificity in the forms of iron accessed by prokaryotes and eukaryotes. Such processes are not generally included in models. Great progress in understanding the links between nitrogen fixation and marine iron cycling have been made in recent years through field and laboratory observations, satellite data analysis, and modeling efforts. The iron requirements for *Trichodesmium* spp., a key nitrogen-fixing cyanobacterium, are approximately 10-fold higher than for most open ocean phytoplankton. Nitrogen fixing diazotrophs have begun to be incorporated into marine ecosystem models. Recent fieldwork strongly suggests that nitrogen fixation in parts of the North Atlantic, where dust inputs are high, is limited by phosphorus, rather than by iron. Satellite data analysis and modeling studies suggest that iron and/or light may be limiting nitrogen fixation rates over much of the remaining tropical/subtropical ocean.

## Carbon and Iron Export

We have a basic understanding of the role of iron in stimulating the onset of phytoplankton blooms, based on bottle experiments and open ocean iron fertilizations. However, we have a much poorer understanding of the fate of carbon produced in the open ocean iron enrichment experiments. It is not apparent, therefore, how iron impacts carbon export, a key variable in regulating atmospheric composition. Discussions at the meeting suggested that small scale (~10 km) fertilization experiments may not achieve the high biomass conditions conducive to carbon export. Horizontal diffusion appears to dilute the patches with unfertilized, low biomass waters and particle concentrations do not reach a point where aggregation and sinking occurs. One recommendation from the Workshop was that future open ocean iron fertilization experiments be conducted in environments such as the Equatorial Pacific where carbon export is easier to observe, and that the experiments be of sufficient scale (~100 km) to enhance the likelihood of observing export.

The workshop discussions also highlighted how little we understand about how dissolved iron is removed from the upper ocean by adsorption and scavenging onto particles. Biological uptake and sinking can remove only a fraction of the dust and coastal iron added each year. The rest must be removed through adsorption/scavenging processes in the upper ocean Little is known about how this key loss process varies with particle concentrations, sinking fluxes, iron and ligand concentrations. Understanding deep ocean iron cycling is critical for modeling ocean biogeochemistry over long timescales.

#### Conclusions

There have been tremendous advances in our understanding of iron cycling in the ocean during the past ten to fifteen years, and we now recognize iron as a keystone regulator of biogeochemical functioning. However, it is also clear that the chemistry of iron can be exceedingly complex. Further, it is unlikely that complex models of iron cycling with many, poorly constrained parameters will lead to successful, prognostic models and a predictive understanding of the effects of iron on ocean biogeochemistry.

A clear message from the modeling community at the meeting was for parameterizations that might lead to relatively simple equations of iron chemistry. At first glance, such requests might appear to be wishful thinking. However, many of the areas where we have developed a reasonable database of reliable observations do lend themselves to simple parameterizations.

One example is the use of Michaelis-Menton equations to predict the impact of iron on community growth rates. Clearly much additional work remains to be done. The key question now is whether additional work will continue to support such basic parameterizations or whether additional work demonstrates that the system is so complicated that simple models will be of little use.

Table 1. A summary of open ocean iron enrichment experiments that have been conducted to date.

IronEx I: equatorial Pacific, 1993. 3-fold increase in chlorophyll. Patch subducted 4 days into the experiment. (Martin et al., 1994, Nature 371, 123-129)

IronEx II: equatorial Pacific, 1996. 10-fold increase in chlorophyll, 90 μatm drawdown in CO2, 5μM drawdown in NO3. (Coale et al., 1996, Nature 383, 495-501)

SOIREE: Pacific sector of Southern Ocean, summer 1999. South of Polar Front. 6-fold increase in chlorophyll, 25  $\mu$ atm drawdown in CO2, 2  $\mu$ M drawdown in NO3. (Boyd et al., 2000, Nature 407, 695-702)

EisenEx-1: Atlantic sector of Southern Ocean, spring 2000. Dispersion into an eddy, 4x increase in chlorophyll. (Strass et al., Abstract OS11L-06 AGU/ASLO 2002 Ocean Sciences Meeting, Honolulu, HI)

SEEDS: western subarctic Pacific Ocean, summer 2001. 40-fold increase in chl, 13  $\mu$ M drawdown in NO3. (Saito et al., Abstract OS41B-07, AGU/ASLO 2002 Ocean Sciences Meeting, Honolulu, HI)

SOFeX: Pacific sector of Southern Ocean, summer 2002. N. and S. of Polar Front. >10x increase in chlorophyll, >40 µatm drawdown in CO2.

(http://www.mbari.org/education/cruises/SOFeX2002/Logbook.htm)