Open Ocean Iron Fertilization for Scientific Study and Carbon Sequestration

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Abstract

The trace element iron has been recently shown to play a critical role in nutrient utilization, phytoplankton growth and therefore the uptake of carbon dioxide from the surface waters of the global ocean. Carbon fixation in the surface waters, via phytoplankton growth, shifts the ocean/atmosphere exchange equilibrium for carbon dioxide. As a result, levels of atmospheric carbon dioxide (a greenhouse gas) and iron flux to the oceans have been linked to climate change (glacial to interglacial transitions). These recent findings have led some to suggest that large scale iron fertilization of the world's oceans may therefore be a feasible strategy for controlling climate. Others speculate that such a strategy could deleteriously alter the ocean ecosystem and still others have calculated that such a strategy would be ineffective in removing sufficient carbon dioxide to produce a sizable and rapid result. Whether iron fertilization has been a viable mechanism controlling climate in the past, and whether it could be useful in the future is a topic of current debate. What is clear from fertilization experiments to date is that they have been effective tools which allowing us to probe the question of the role of iron in controlling phytoplankton growth, nutrient cycling and the flux of carbon from the atmosphere to the deep sea.

Introduction

Phytoplankton growth in the oceans requires optimal physical, chemical and biological factors which are distributed inhomogenously in space and time. Because carbon, primarily in the form of the bicarbonate ion and sulfur as sulfate, are abundant throughout the water column, the major plant nutrients in the ocean commonly thought to be critical for phytoplankton growth are those that exist at the micromolar level such as nitrate, phosphate and silicate (Dugdale, 1976). These, together with carbon and sulfur form the major building blocks for biomass in the sea. As fundamental cellular constituents, they are generally thought to be taken up and remineralized in constant ratios to one another.

The vertical distribution of the major nutrients typically show surface water depletion and increasing concentrations with depth. Vertical profiles reflect the processes of phytoplankton uptake within the euphotic zone and remineralization of sinking planktonic debris via microbial degradation, leading to increased concentrations in the deep sea. Given favorable growth conditions, the nutrients at the surface may be depleted to zero. The rate of phytoplankton production of new biomass, and therefore the rate of carbon uptake is controlled by the resupply of nutrients to the surface waters, usually via the upwelling of deep waters. Upwelling occurs over the entire ocean basin at the rate of approximately 4 m per year but increases in coastal and regions of divergent surface water flow reaching average values of 15 to 30 or greater (Broecker and Peng, 1982). Thus, those regions of high nutrient supply or persistent high nutrient concentrations are thought to be most important in terms of carbon removal.

Carbon flux from the surface waters to depth take place via a process known as the biological pump (Figure 1).

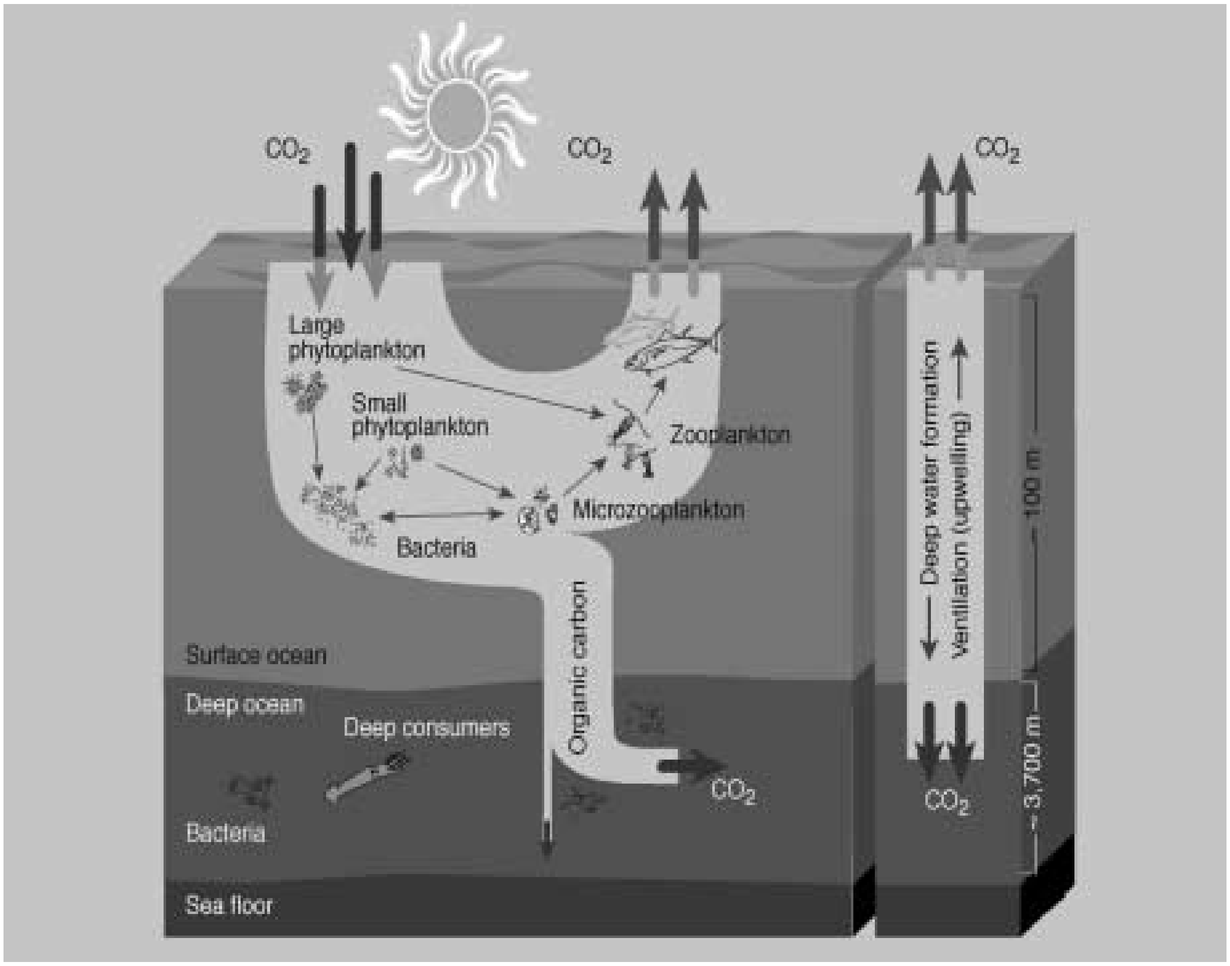

Figure 1. A schematic representation of the biological pump. Figure courtesy of Z. Johnson and Nature Magazine, October 12, 2001.

In this case the carbon fixed by phytoplankton is consumed by grazers or sinks directly from the surface waters. The flux of organic carbon decreases with depth due to microbial remineralization and decomposition. Because deeper waters do not ventilate with the atmosphere as readiliy as surface waters, the effectiveness of the biological pump in removing carbon is directly dependent upon the depth to which carbon is removed (Figure 2).

Although both nitrogen and phosphorous are required at nearly constant ratios characteristic of deep water, nitrogen has generally been thought to be the limiting nutrient in seawater rather than phosphorous (Codispoti, 1989; Smith, 1984). This idea has been based on two observations. 1) Selective enrichment experiments and 2) Surface water distributions. When ammonia and phosphate are added to seawater in grow out experiments, phytoplankton growth increases in the ammonia addition and not in the phosphate addition, thus indicating that reduced nitrogen and not phosphorus is limiting. Also, when surface water concentration of nitrate and

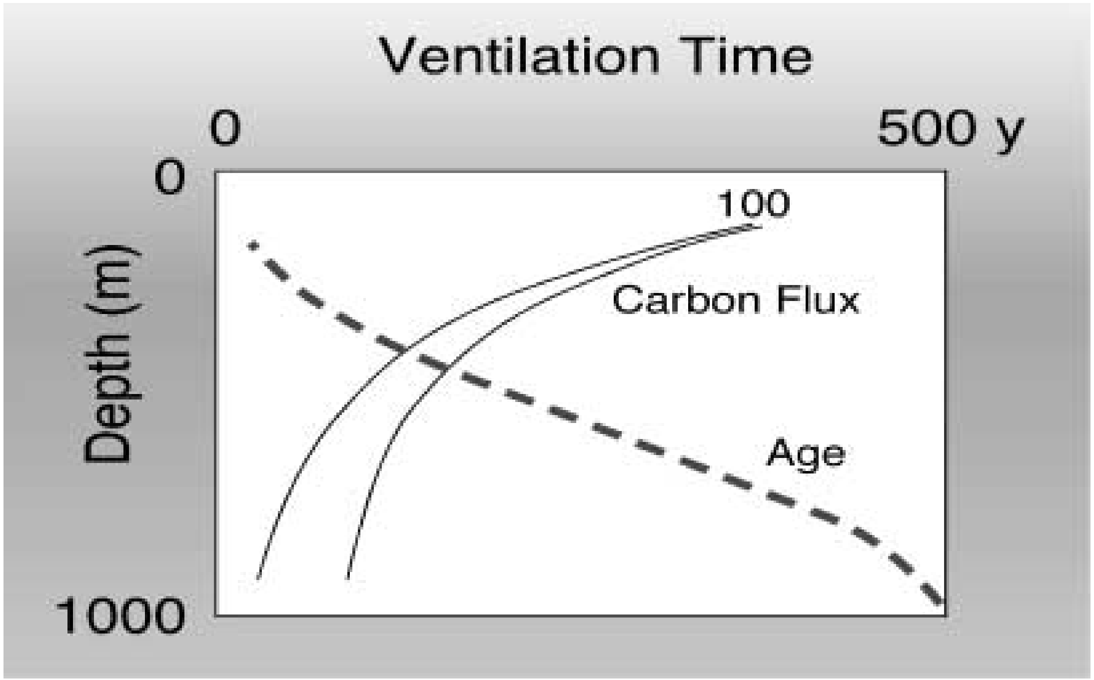

Figure 2. Schematic representation of carbon flux and surface water ventilation time

phosphate are plotted together, it appears there is still residual phosphate after the nitrate has gone to zero.

The notion of nitrogen limitation seems counter intuitive when one considers the abundant supply of dinitrogen in the atmosphere. Yet, this nitrogen gas is kinetically unavailable to most phytoplankton because of the large amount of energy required to break the triple bond which binds the dinitrogen molecule. Only those organisms capable of nitrogen fixation can take advantage of this form of nitrogen and reduce atmospheric N2 to biologically available nitrogen in the form of urea and ammonia. This is, energetically, a very expensive process requiring specialized enzymes (nitrogenase, an iron-requiring enzyme), an anaerobic micro environment and large amounts of reducing power in the form of electrons generated by photosynthesis. Although there is currently the suggestion that nitrogen fixation may have been underestimated as an important geochemical process, the major mode of nitrogen assimilation, giving rise to new plant production in surface waters, is thought to be nitrate uptake.

High Nitrate Low Chlorophyll (HNLC) Regions

The HNLC regions are thought to represent about 20% of the areal extent of the world's oceans. These are generally regions characterized by more than 2 micromolar nitrate and less than 0.5 micrograms chlorophyll a per liter. The major HNLC regions are shown in Figure 3 and represent the Subarctic Pacific, large regions of the Eastern Equatorial Pacific and the Southern ocean. These HNLC regions persist in areas which have high macronutrient concentrations, adequate light and physical characteristics required for phytoplankton growth, but have very low plant biomass. Several studies of zooplankton grazing and phytoplankton growth in these HNLC regions, particularly the Subarctic Pacific, confirm the hypothesis that grazers control phytoplankton production in these waters. Recent physiological studies, however, indicate that

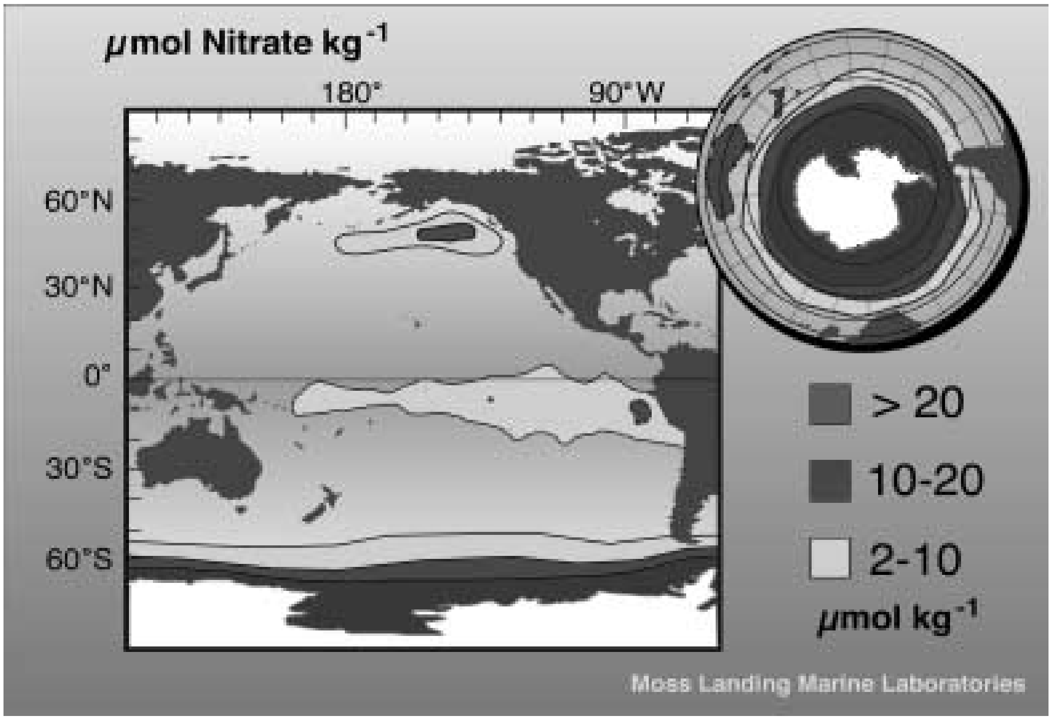

Figure 3. Representation of the major HNLC regions of the world's oceans.

phytoplankton growth rates in these regions are suboptimal as is the efficiency with which phytoplankton harvest light energy. These observations indicated that phytoplankton growth may be limited by something other than (or in addition to) grazing. Specifically, these studies implicate the lack of sufficient electron transport proteins, symptomatic of iron deficiency.

The Role of Iron

Iron is a required micronutrient for all living systems. Because of it's d-orbital configuration, iron readily undergoes redox transitions between Fe II and Fe III at physiological redox potentials. For this reason, iron is particularly well suited to many enzyme and electron carrier proteins. The genetic sequence coding for many iron containing electron carriers and enzymes are highly conserved indicating iron and iron containing proteins were key features of early biosynthesis. Many primitive aquatic and terrestrial organisms have subsequently evolved the ability to sequester iron through the elaboration of specific iron-III binding ligands, known as siderophores. Recently, evidence for siderophore production has been found in several marine dinoflagellates and bacteria and some scientists have recently detected similar compounds in seawater (Rue and Bruland, 1997, Van den Berg, 1995).

Today, iron exists in seawater at extremely small concentrations. Due to both inorganic precipitation and biological uptake, typical surface water values are on the order of 20 picomolar. Iron concentrations in the oceans increase with depth, in much the same manner as the major plant nutrients (Figure 4).

The discovery that iron concentrations in surface waters is so low and shows a nutrient like profile, led some to speculate that iron availability limits plant growth in the oceans. This notion has been tested in bottle enrichment experiments throughout the major HNLC regions of the world's oceans. These experiments have demonstrated dramatic phytoplankton growth and

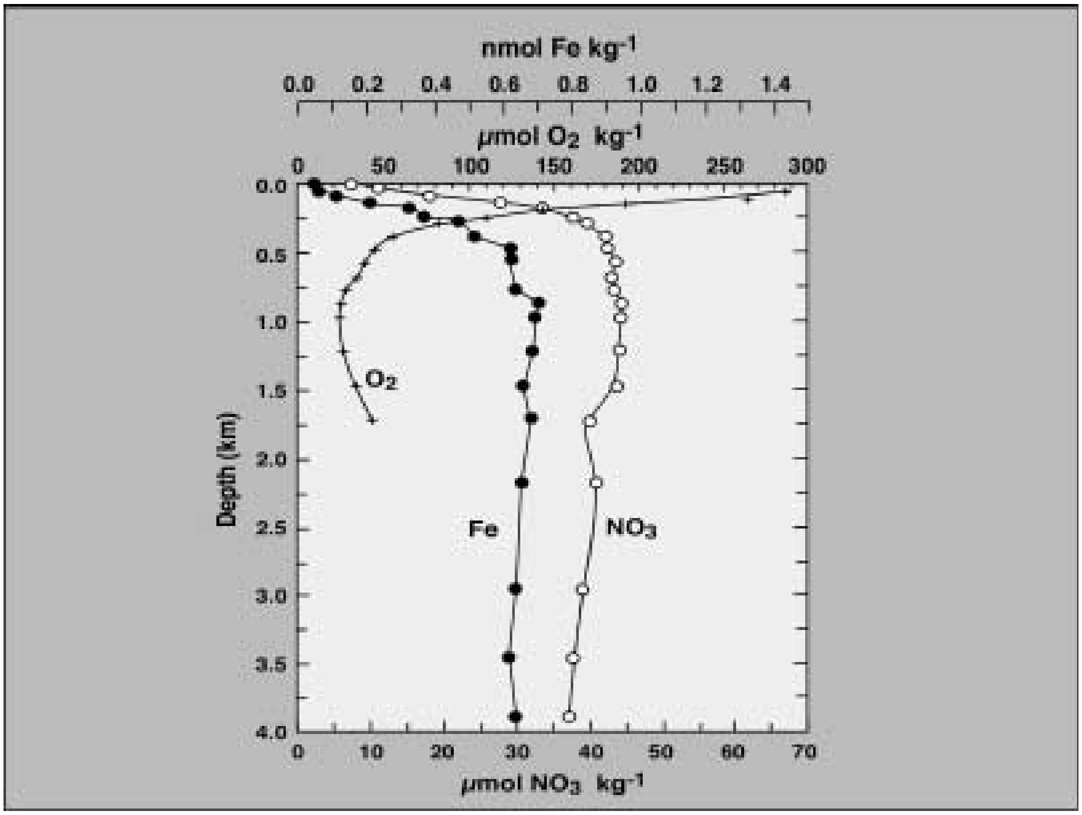

Figure 4. Vertical profiles of iron, oxygen and nitrate from the central north Pacific.

nutrient uptake upon the addition of iron relative to control experiments where no iron was added.

Criticism that such small scale, enclosed experiments may not accurately reflect the response of the HNLC system at the level of the community has led to several large scale iron fertilization experiments in the equatorial Pacific and Southern Ocean. These have been some of the most dramatic oceanographic experiments of our times and have led to a profound and new understanding of ocean systems.

Open Ocean Iron Enrichment

The question of iron limitation was brought into sharp scientific focus with a series of public lectures, reports by the US National Research Council, papers, special publications and popular articles between 1988 and 1991. What was resolved was the need to perform an open ocean enrichment experiment in order to definitively test the hypothesis that iron limits phytoplankton growth, nutrient and carbon dioxide uptake in HNLC regions. Yet, such an experiment posed sever logistical challenges and had never been conducted.

Experimental Strategy

The mechanics of producing an iron enriched experimental patch and following it over time was developed in four release experiments in the equatorial Pacific (IronEx I and II, Martin et al., 1994; Coale et al., 1996, 1998) and more recently in the Southern Ocean (SOIREE, Boyd et al., 2000). A similar strategy was also employed in the recent Eisenex experiments in the Atlantic sector of the Southern Ocean. All of these strategies were developed in order to address certain scientific questions and were not designed as preliminary to any geoengineering effort.

Experimental Measurements

In addition to the tactical measurements and remote sensing techniques required to track and ascertain the development of the physical dynamics of the enriched patch, a number of measurements have been made to track the biogeochemical development of the experiment. These have typically involved a series of both underway measurements made using the ships flowing seawater system or towed fish. In addition, discrete measurement are made in the vertical dimension at every station occupied both inside and outside of the fertilized area. These measurements include, temperature, salinity, fluorescence (a measure of plant biomass), transmissivity (a measure of suspended particles), oxygen, nitrate, phosphate, silicate, carbon dioxide partial pressure, pH, alkalinity, total carbon dioxide, iron binding ligands, Th-234:U-238 radioisotopic disequilibria (a proxy for particle removal), relative fluorescence (indicator of photosynthetic competence), primary production, phytoplankton and zooplankton enumeration, grazing rates, nitrate uptake, particulate and dissolved organic carbon and nitrogen. These parameters allows for the general characterization of both the biological and geochemical response to added iron. From the results of the equatorial enrichment experiments (IronEx I and II) and the Southern Ocean Iron Enrichment Experiment (SOIREE), several general features have been identified.

Findings to Date

Biophysical Response

The experiments to date have focused on the High Nitrate, Low Chlorophyll (HNLC) areas of the world's oceans, primarily in the Subarctic, Equatorial Pacific and Southern Ocean. In general when light is abundant many researchers find that HNLC systems are Fe limited. The nature of this limitation is similar between regions but manifests itself at different levels of the trophic structure in some characteristic ways. In general, all members of the HNLC photosynthetic community are physiologically limited by iron availability. This observation is based primarily on the examination of the efficiency of photosystem II, the light harvesting reaction centers. At ambient levels of iron, light harvesting proceeds at sub-optimal rates. This has been attributed to the lack of iron dependent electron carrier proteins at low iron concentrations. When iron concentrations are increased by sub-nanomolar amounts, the efficiency of light harvesting rapidly increases to maximum levels. Using fast repetition rate fluorometry and non-heme iron proteins, researchers have described these observations in detail (Greene et al., 1991; Kolber et al., 1994; Behrenfeld et al., 1996; La Roche et al., 1996). What is notable about these results is that iron limitation seems to affect the photosynthetic energy conversion efficiency of even the smallest of phytoplankton (Cavender-Bares, et al., 1999). This has been a unique finding which stands in contrast to the hypothesis that, because of diffusion, smaller cells are not iron limited, but larger cells are.

Nitrate Uptake

As discussed above, iron is also required for the reduction (assimilation) of nitrate. In fact a change of five oxidation states is required between nitrate and the reduced forms of nitrogen found in amino acids and proteins. Such a large and energetically unfavorable redox process is only made possible by substantial reducing power (in the form of NADPH) made available through photosynthesis and active nitrate reductase, an iron requiring enzyme. Without iron, plants cannot take up nitrate efficiently. This provided original evidence implicating iron deficiency as the cause of the HNLC condition. When phytoplankton communities are relieved from iron deficiency, specific rates of nitrate uptake increase. This has been observed in both the equatorial Pacific and the Southern Ocean using isotopic tracers of nitrate uptake and conversion (Cochlan et al., submitted, Boyd et al., 2000). In addition the accelerated uptake of nitrate has been observed in both the mesoscale iron enrichment experiments to date: IronEx and SOIREE.

Growth Response

When iron is present, phytoplankton growth rates increase dramatically (Coale, et al., 1996; Fitzwater et al., 1996). These and other experiments, over widely differing oceanographic regimes, have demonstrated that, when light and temperature are favorable, phytoplankton growth rates in HNLC environments increase to their maximum at dissolved iron concentrations generally below 0.5 nM. This observation is significant in that it indicates that phytoplankton are adapted to very low levels of iron and they do not grow faster if given more than half a nanomolar of iron. Given that there is still some disagreement within the scientific community about the validity of some iron measurements, this phytoplankton response provides a natural, environmental and biogeochemical benchmark against which to compare results.

The iron induced transient imbalance between phytoplankton growth and grazing in the equatorial Pacific during IronEx II resulted in a 30 fold increase in plant biomass (Coale et al., . Similarly, a six fold increase was observed during the SOIREE experiment in the Southern Ocean. These are perhaps the most dramatic demonstrations of iron limitation of nutrient cycling, and phytoplankton growth to date and has fortified the notion that iron fertilization may be a useful strategy to sequester carbon in the oceans.

Heterotrophic Community

As the primary trophic levels increase in biomass, growth in the small microflagellate and heterotrophic bacterial communities increase in kind. It appears that these consumers of recently fixed carbon (both particulate and dissolved) respond to the food source and not necessarily the iron (although some have been found to be iron limited). Because their division rates are fast, heterotrophic bacteria, ciliates and flagellates can rapidly divide and respond to increasing food availability to the point where the growth rates of the smaller phytoplankton can be overwhelmed by grazing (Barbeau et al., 1996; Hall and Safi, 2000). Thus there is a much more rapid turnover of fixed carbon and nitrogen in iron replete systems. M. Landry and coworkers (Landry et al., 2000) have documented this in dilution experiments conducted during IronEx II. These results appear to be consistent with the recent SOIREE experiments as well.

Nutrient Uptake Ratios

An imbalance in production and consumption, however, can arise at the larger trophic levels. Because the reproduction rates of the larger micro- and meso-zooplankton are long with respect to diatom division rates, iron replete diatoms can escape the pressures of grazing on short time scales (weeks). This is thought to be the reason why, in every iron enrichment experiment, diatoms ultimately dominate in biomass. This result is important for a variety of reasons. It suggests that transient additions of iron would be most effective in producing net carbon uptake and it implicates an important role of silicate in carbon flux. The role of iron in silicate uptake has been studied extensively by Franck et al. (2000). Our results, together with those of Takeda and coworkers (Takeda and Obata, 1995), show that iron alters the uptake ratio of nitrate and silicate at very low levels. This is thought to be brought about by the increase in nitrate uptake rates relative to silica.

Organic Ligands

Consistent with the role of iron as a limiting nutrient in HNLC systems is the notion that organisms may have evolved competitive mechanisms to increase iron solubility and uptake. In terrestrial systems this is accomplished using extracellularly excreted or membrane bound siderophores. Similar compounds have been shown to exist in seawater where the competition for iron may be as fierce as it is on land. In open ocean systems where it has been measured, iron binding ligand production increases with the addition of iron. Whether this is a competitive response to added iron or a function of phytoplankton biomass and grazing is not yet well understood. Yet, this is an important natural mechanism for reducing the inorganic scavenging of iron from the surface waters and increasing iron availability to phytoplankton. Recent studies (Van den Berg, 1995; Trick and Wilhelm, 1995; Rue and Bruland, 1997; Croot et al., in prep) have advanced considerably our understanding of these ligands, their distribution and their role in ocean ecosystems.

Carbon Flux

It is the imbalance in the community structure which gives rise to the geochemical signal. Whereas iron stimulation of the smaller members of the community may result in chemical signatures such as an increased production of dimethylsulfionproprionate (DMSP), (Turner et al., 1996), it is the stimulation of the larger producers which decouples the large cell producers from grazing and results in a net uptake and export of nitrate, carbon dioxide and silicate.

The extent to which this imbalance results in carbon flux, however, has yet to be adequately described. The inability to quantify carbon export has primarily been a problem of experimental scale. Even though mesoscale experiments have, for the first time, given us the ability to address the effect of iron on communities, the products of surface water processes and the effects on the midwater column have been difficult to track. For instance, on the IronEx II experiment, a time series of the enriched patch was diluted by 40% per day and is described in a manuscript by Nightingale et al., 2000. The dilution was primarily in a lateral (horizontal/isopycnal) dimension. Although some correction for lateral dilution can be made, our ability to quantify carbon export is dependent upon the measurement of a signal in waters below the mixed layer or from an un-eroded enriched patch. Current data from the equatorial Pacific showed that the IronEx II experiment advected over six patch diameters per day. This means that at no time during the experiment were the products of increased export reflected in the waters below the enriched area. A transect through the IronEx II patch is shown in Figure 5. This figure indicates the massive production of plant biomass with a concomitant decrease in both nitrate and carbon dioxide.

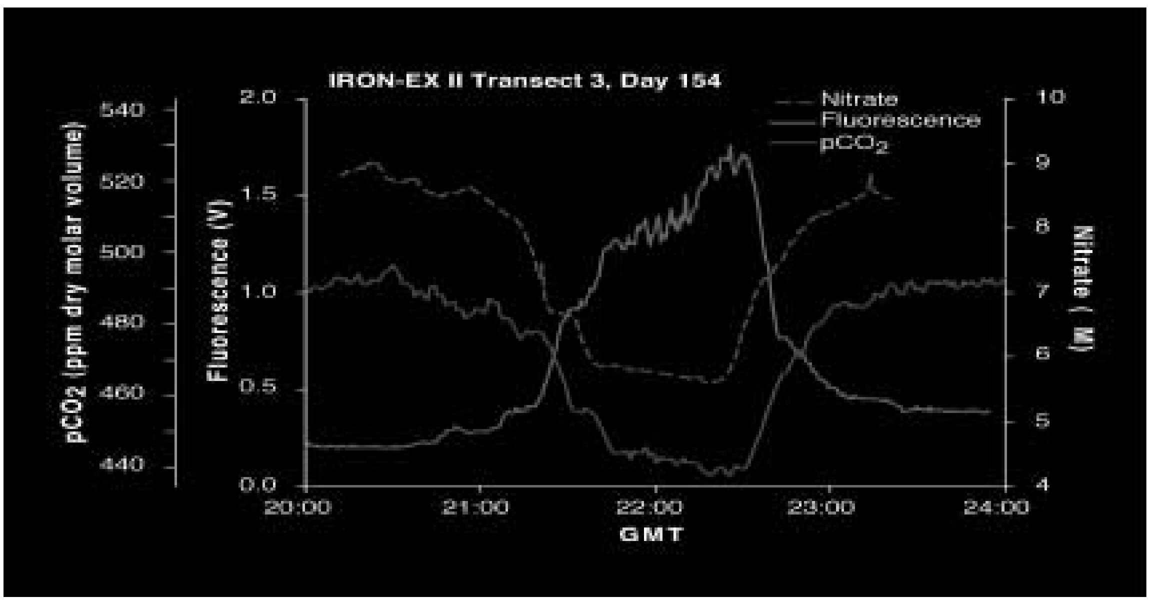

Figure 5. Geochemical response of iron enrichment during IronEx II.

The results from the equatorial Pacific, when corrected for dilution suggest that about 2,500 tons of carbon were exported from the mixed layer over a seven day period. These results are preliminary and subject to more rigorous estimates of dilution and export production, but they do agree favorably with estimates based upon both carbon and nitrogen budgets. Similarly, thorium export was observed in this experiment confirming some particle removal.

The results of the recent SOIREE experiment were similar in many ways but were not as definitive with respect to carbon flux. In this experiment biomass increased by six fold, nitrate was depleted by 2 micromolar and carbon dioxide by 35-40 microatmospheres. This was a greatly attenuated signal relative to IronEx II. Colder water temperatures likely led to slower rates of production and bloom evolution and there was no observable carbon flux.

Original estimates of carbon export in the Southern Ocean based on the iron induced efficient utilization of nitrate, suggest that as much as 1.8 billion tons of carbon could be removed annually. These estimates of carbon sequestration have been challenged by some modelers yet all models lack important experimental parameters which will be measured in upcoming experiments.

Remaining Questions

There are a multitude of questions remaining regarding the role of iron in shaping the nature of the pelagic community. The most pressing question is: Does iron enrichment accelerate the downward transport of carbon from the surface waters to the deep sea? More specifically: How does iron affect the cycling of carbon in HNLC, LNLC and coastal systems. Recent studies indicate that coastal systems may be iron limited and the iron requirement for nitrogenase activity is quite large suggesting iron may limit nitrogen fixation, but there have been limited studies to test the former and none to test the latter. If iron does stimulate carbon uptake, what are the temporal and spatial scales over which this fixed carbon may be remineralized? This is crucial to predicting whether fertilization is an effective carbon sequestration mechanism and is illustrated in Figure 2.

Given these considerations, the most feasible way to understand and quantify carbon export from an enriched water mass is to increase the scale of the experiment such that both lateral dilution and sub-mixed layer relative advection is small with respect to the size of the enriched patch. For areas such as the equatorial Pacific, this would be very large (100s of kilometers on a side). For other areas, this could be much smaller.

The focus of the IronEx and SOFeX experiments has been from the scientific perspective, but this focus is shifting towards the application of iron enrichment as a carbon sequestration strategy. We have come about rapidly from the perspective of trying to understand how the world works, to one of trying to make the world work for us. Several basic questions remain regarding the role of natural or anthropogenic iron fertilization on carbon export. Some of the most pressing questions are: What are the best proxies for carbon export? How can carbon export best be verified? What are the long term ecological consequences of Fe enrichment on 1) Surface Water Community Structure? 2) Midwater Processes? 3) Benthic Processes? Even with these answers, there are others which would need to be addressed prior to any serious consideration of iron fertilization as an ocean carbon sequestration option.

Simple technology is sufficient to produce a massive bloom. The technology required for either a large scale enrichment experiment or for purposeful attempts to sequester carbon, is readily available. Ships, aircraft (tankers and research platforms), tracer technology, a broad range of new Autonomous Underwater Vehicles (AUVs) and instrument packages, Lagrangian buoy tracking systems, together with aircraft and satellite remote sensing systems and a new suite of chemical sensors/in situ detection technologies are all available, or are being developed at this time. Industrial bulk handling equipment is available for large scale implementation. The big questions, however, are larger than the technology.

With a slow start, the notion of both scientific experimentation through manipulative experiments, as well as the use of iron to purposefully sequester carbon is gaining momentum. There are now national, international, industrial, and scientific concerns willing to support larger scale experiments. The materials required for such an experiment are inexpensive and readily available even as industrial byproducts (paper, mining, steel processing).

Given the concern over climate change and the rapid modernization of large developing countries (China, India, etc...) there is a pressing need to address the increased emission of green house gasses. Through the implementation of the Kyoto accords or other international agreements to curb emissions (Rio), financial incentives will reach into the multi-billion dollar level annually. Certainly there will soon be an overwhelming fiscal incentive to investigate, if not implement purposeful open ocean carbon sequestration trials.

A Societal Challenge

The question is not whether we have the capability of embarking upon such an engineering strategy, the question is whether we have the collective wisdom to responsibly negotiate such a course of action. Have we as an international community first tackled the difficult but obvious problem of overpopulation and implemented alternative energy technologies for transportation, industry and domestic use?

There are other social questions which arise as well such as: Is it appropriate to use the ocean commons for such a purpose? What individuals, companies or countries would derive monetary compensation for such an effort and how would this be decided?

It is clear that there are major science investigations and findings which can only benefit from large scale open ocean enrichment experiments, but certainly a large scale carbon sequestration effort should not proceed without a clear understanding of both the science and the answers to the questions above.

American Society of Limnology and Oceanography (ASLO) Workshop

To address some of these questions, ASLO recently convened a workshop (April 23-25, 2001, Washington DC) to bring together scientists, representatives from industry, policy makers and private groups interested in ocean fertilization as a carbon sequestration option. Although the interests of the group were diverse, a consensus statement is emerging regarding three important questions. A summary of these questions and excerpts from an emerging concensus statement appear below:

I. Can atmospheric CO_2 be sequestered through ocean fertilization, and if so, what are the consequences?

On the basis of available information, it was felt that the community cannot dismiss ocean fertilization with iron as an option. However, numerical models predict that it would at the very best reduce the expected increase of atmospheric CO_2 by a small percentage. Achieving this degree of sequestration would entail major alterations of the ecosystem, such as changes in food web structure and biogeochemical cycles. These changes will have unknown consequences, some of which will be inherently unpredictable. More broadly, there are profound deficiencies in our understanding of a broad range of ocean-atmosphere processes that must be addressed in order to assess the role of the oceans in climate regulation both through natural (via atmospheric dust) and intentional iron enrichment.

II. What guidelines would ensure scientific integrity, avoid conflict of interest and protect the public trust in the relationship among scientists, industry and government?

Recognizing that the global ocean common requires special governance, and that both private and public resources will be used for carrying out the necessary research, a partnership must be created among academic scientists, industry, and government. Examples for partnerships may come from the biomedical field, other areas of public policy, the Antarctic Treaty, and various agreements that govern the use of the sea.

III. What would be the appropriate governance structure for ocean fertilization?

No appropriate intergovernmental governance structure has been identified with specific authority for ocean fertilization — both experimental and operational — although many articles in existing structures may be applicable to some portion of the ocean fertilization issue. International agreements on activities in the high seas have advanced the principles of a precautionary approach, polluter pays, transgenerational equity, and sharing knowledge and benefits.

Based upon the answers to these questions, several recommendations emerged:

ASLO and other partners should initiate plans to convene an internationally sponsored symposium to address the role of marine productivity in climate change, including natural events and intentional manipulation of the system.

In regards to the formation of public/private partnerships to further investigate ocean carbon sequestration via open ocean fertilization, the accepted standards such as transparency, public access to data, and peer review, were recommended. Partnerships must include:

- Shared responsibility to advance the understanding of carbon cycle science
- Environmental assessment should be required by governments, and notice given to potentially affected citizens
- Liability for foreseen and unforeseen circumstances must be addressed

Review and oversight of intentional ocean fertilization should occur through an international mechanism.

The international scientific community should start now to develop a code of practice for guiding intentional ocean fertilization. ASLO should investigate avenues (e.g. approach SCOR) to initiate this.

To initiate an international mechanism for oversight of fertilization, the results of this workshop should be disseminated to the secretariats of the appropriate international, intergovernmental and government organizations for their consideration and action.

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