

Ocean Iron Fertilization Conceptual Model

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The fertilization of regions of the ocean that are deficient in iron but otherwise replete with macronutrients has been under scientific investigation since the essential role of iron in regulating primary production in these regions was hypothesized in the late 1980's. Mesoscale ocean experiments have shown that iron fertilization of these extraordinary high-nutrient areas can lead to significant increases in primary production, reductions of CO₂ in the surface layer of the sea, and potentially add to the ocean's essential role in atmospheric CO₂ attenuation. While the results of these experiments are intriguing, the spatial and temporal extent of ocean iron fertilization (OIF) experiments to date has been limited. Key questions remain, and there are many theoretical and practical reasons to explore the larger-scale response in a representative iron-deficient region of the ocean to natural and designed fertilization.

Climos, interested in facilitating ways to address the problem of global warming and responding to financial incentives associated with market-based regulatory and voluntary actions, has plans underway to increase the scale of the OIF trial and test the ability of OIF to sequester larger amounts of atmospheric CO₂. At the same time, Climos is responsive to questions that have been raised regarding the effectiveness of OIF as a sequestration technique and potential ecological effects of stimulating primary production in marine waters. A detailed environmental analysis of larger-scale OIF, commissioned by Climos, is underway. The cornerstone of this analysis is the development of a Conceptual Model of OIF that will be prepared prior to commencement of the proposed project.

The Conceptual Model will describe and graphically represent existing knowledge on biogeochemical processes that control and are affected by increasing atmospheric CO₂ concentrations. Emphasis will be placed on utilizing the latest available scientific information to describe the level of understanding of these processes in the marine environment. This information includes the results of the twelve mesoscale ocean iron fertilization experiments that have opened a new field of investigation and contributed new insights into the understanding of the biogeochemistry of the ocean's mixed layer. Over 450 scientific papers have

been published on the results of these experiments and the extension of these results through numerical modeling. The OIF conceptual model will provide a synthesis of this information and will be used to identify and evaluate the environmental issues associated with proposed ocean iron fertilization activities.

The OIF Conceptual Model is being developed around the description of the underlying cycles that are driven by and affect key biogeochemical processes. The description of the global carbon cycle and human impacts on the cycle through increased CO₂ emissions provides the foundation for the conceptual model. The carbon fluxes that link the oceans to current and historic atmospheric CO₂ concentrations are described and provide a basis for the discussion of proposed mitigation actions to reduce atmospheric CO₂ concentrations. The chemical, biological and physical processes that interact in the sequestration of organic carbon - the ocean biological pump - are described, and a series of questions regarding the role of nutrient cycling and the cycling of organic matter in the mixed layer of the ocean are addressed.

The following description of the global iron cycle provides an example of how these underlying cycles will be presented in the OIF Conceptual Model.

Ecosystem Component: Ocean Iron Cycle

The operation of the ocean iron cycle (Figure 1) is largely determined by two basic facts about this trace element. They are i) the extremely low solubility in seawater of its stable Fe^{III} oxidation state and ii) the inescapable biological need for iron. As a consequence, biota must adapt to, and ultimately compete with, largely abiotic, geochemical processes, making the ocean iron cycle thoroughly "biogeochemical" in character.

The largest flux in the ocean iron cycle is riverine transport, which carries up to 960 Tg per year to the ocean (Table 1). However, nearly all of the Fe discharged by rivers occurs in particulate forms that are deposited on continental shelves and other nearshore environments. Only 0.2 percent of this flux, or 1.5 Tg yr⁻¹, is in dissolved form and therefore available to be transported to the open ocean to sustain

phytoplankton growth. Re-dissolution of particulate iron in continental shelf sediments releases a similar flux of dissolved Fe back to the water column, but the fraction of this flux that reaches the photic zone is uncertain and may be as low as 2.5% (Johnson *et al.*, 2004). Coastal upwelling events can supply Fe by re-suspending fine particles from shelf sediments as well that in turn dissolve and provide much of the iron necessary to sustain the growth of phytoplankton in some coastal waters (Johnson *et al.*, 1999). Due to the high productivity of the coastal ocean, most of this dissolved Fe is trapped on continental shelves. Still, that transport of dissolved Fe into the open ocean

occurs is readily apparent from the decrease in surface dissolved Fe concentrations along oceanographic transects away from coastal regions (Elrod *et al.*, 2004). Since the elevated dissolved Fe is only detectable for several hundred kilometers, the vast majority of the ocean is unaffected by Fe of coastal origin.

The primary source of Fe to open ocean surface waters is the wind-driven transport of dust from the continents (Table 1). Such dust originates in arid and semi-arid regions where past or seasonal fluvial erosion generates wind-erodible material. Fine particles (~2 μm in diameter)

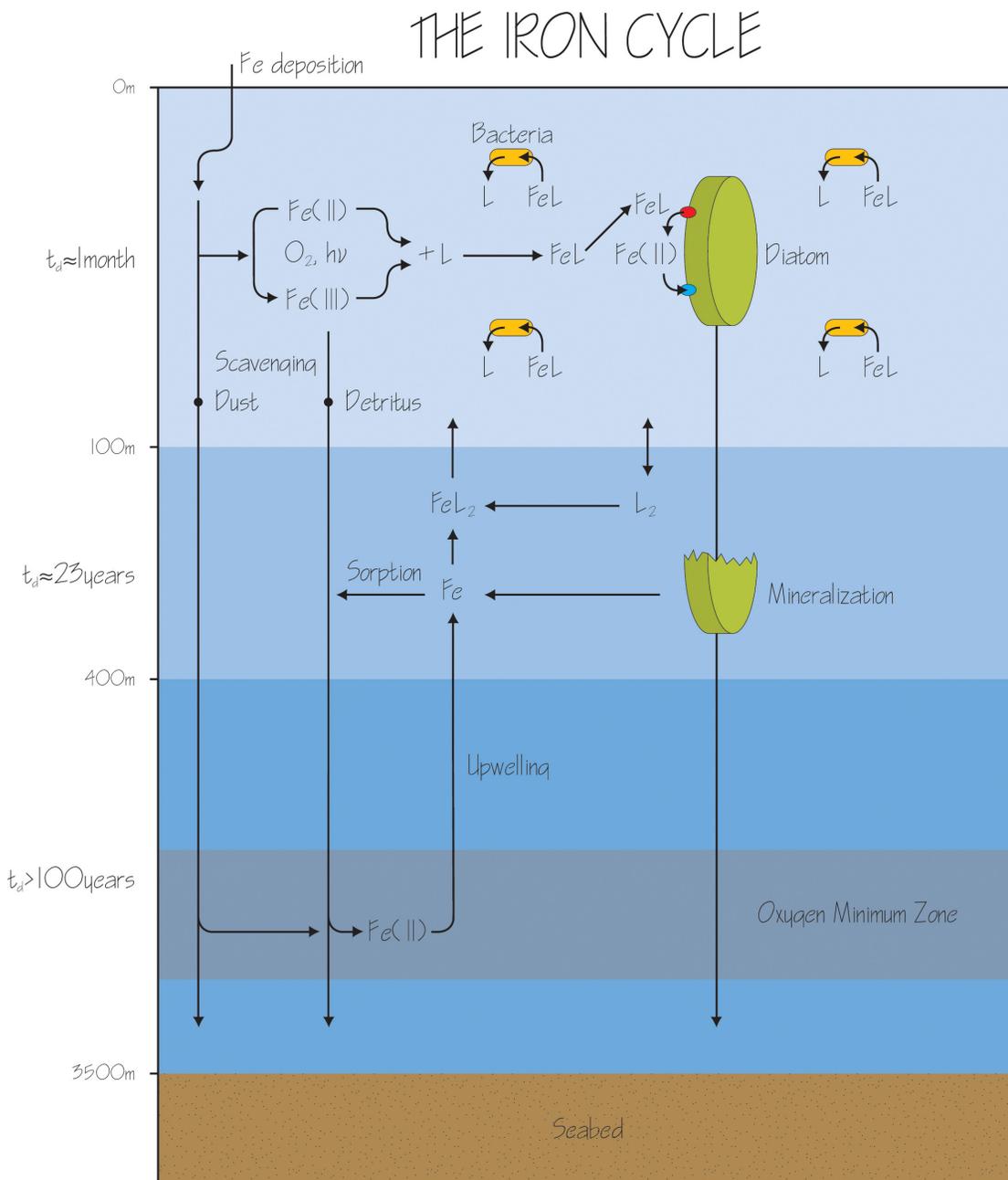


Figure 1 Major processes in the ocean iron cycle. Iron enters and leaves the open ocean largely in particulate forms. Biological processes deplete dissolved iron in the surface ocean while the balance between mineralization and abiotic scavenging (sorption) control its concentrations at depth. When the oxygen minimum layer is nearly devoid of oxygen, the balance between scavenging and dissolution shifts towards much greater reductive dissolution of particulate iron within that layer.

are readily entrained by vertical atmospheric motions that carry the material to high altitude (3-7 km) where it can be transported thousands of kilometers before encountering atmospheric conditions – precipitation or low wind speed – that cause it to be deposited onto the ocean’s surface (Jickells *et al.*, 2005). During transport, factors such as cloud water acidity, sulfate, and sunlight affect chemical reactions that transform less soluble iron oxides into more soluble amorphous iron forms (Fan *et al.*, 2006).

Dust particles transport about 16 Tg of Fe per year to the ocean. Once in the surface layer, a few percent (1-10%) of the Fe in the particles dissolves (Table 1). This dissolution is limited by the fact that the pH of seawater falls almost exactly at the solubility minimum of ferric (Fe^{III}) oxides (Waite, 2001). The extent of dust Fe dissolution can be significantly enhanced by photochemical reduction of the Fe^{III} and by the presence of strong Fe-binding organic chelators in the seawater. Of the resultant dissolved iron in surface waters, most occurs in the Fe^{III} oxidation state bound to strong chelators, but light-driven chemical reduction leads to diurnal variations in concentrations of uncomplexed iron, or Fe’ (Fan, 2008).

Biotic uptake is the dominant process that consumes dissolved iron in the surface ocean. Uncomplexed Fe’ is available to the widest variety of organisms (Hudson and Morel, 1990), but generally constitutes a very small fraction

of the dissolved Fe. Many microbes are able to directly take up chelated Fe (FeL) and actually produce some of the chelating molecules present in order to solubilize Fe and/or outcompete other organisms for Fe. Larger phytoplankton are known to overcome low supplies of Fe’ via extracellular enzymatic reduction of chelated Fe to form more available Fe^{II} species (Maldonado *et al.*, 2001), (See Figure 1). The competition between uptake by living organisms and scavenging by particles causes Fe to have a short residence time of the order of a month in the surface ocean.

Biological uptake also depletes Fe concentrations at the ocean surface, just as major nutrients like N and P are depleted in most of the world ocean. For this reason, iron cycling in the upper ocean can be characterized by Redfield-type stoichiometries, albeit ones that differ between organisms. The lowest requirement for Fe is exhibited by diatoms, which need ~0.000025 mole Fe per mole carbon. Oceanographic studies (de Jong *et al.*, 2007) indicate that picoplankton require nearly ten-fold higher amounts of Fe, or 0.00002 mole Fe per mole C. N₂-fixing organisms, are believed to have the greatest Fe requirement, 0.000025 mole Fe per mole C, although Fe requirements have only been characterized to date for a few diazotrophic species. The similarity of the marine chemistry of Fe to major nutrients extends as well to its extensive recycling via grazing on picoplankton within the surface layer and to its re-mineralization in parallel with C, N, and P in

Table I
Iron inputs to surface waters of the coastal and open ocean.

Source of Iron	Annual Flux (Tg yr ⁻¹) ^a
Inputs to Coastal Ocean Surface Waters	
Riverine particles	625 to 962
Glacial sediments	34 to 211
Resuspension by upwelling	? ^c
Coastal erosion	8
Riverine dissolved	1.5
Diffusion from shelf sediments	>0.1 ^b
Dissolution of re-suspended particles	? ^c
Inputs to Open Ocean Surface Waters	
Wet and Dry Deposition of Dust Particles	16
Dissolution of Dust Particles	0.2-0.3
Dissolved transport from shelf	Low
Upwelling from ocean interior	Low

^a Except as noted from Jickells *et al.* (2005).

^b Elrod *et al.* (2004)

^c Johnson *et al.* (2001)

sinking biogenic particles. The net result is that Fe exhibits a nutrient-like concentration profile in the upper 1000 m of the ocean (Martin and Gordon, 1988).

Iron does not, however, behave like N or P at greater depths (Johnson *et al.*, 1999). Instead of simply accumulating re-mineralized Fe as the abyssal ocean circulation transports water through the Atlantic and Indo-Pacific Ocean basins, Fe is continually removed at depth via *scavenging*. *Scavenging* is a generic term used to describe the processes – adsorption to particles and precipitation as insoluble minerals – by which metals such as Al, Fe, and Th are removed from the ocean interior. Because it strongly hydrolyzes like Al and Th, Fe can also be strongly scavenged, yet its concentrations do not decrease with depth like Al and Th. This exceptional behavior is caused by i) the presence of Fe-chelating molecules or organic “ligands” in seawater that keep higher levels of Fe in solution and ii) by the reversibility of its main scavenging process, precipitation of the thermodynamically-favored oxidation state (Fe^{III} or ferric) as iron oxides. Thus, deep water iron concentrations do not increase as much as N and P between the Atlantic and Pacific basins.

One additional process within the ocean interior exerts a potentially important influence on its concentrations: microbial Fe^{III} reduction in oxygen minimum zones (Moore *et al.*, 2006). At very low oxygen concentrations, bacteria respire using nitrate and iron oxides. Since the solubility of reduced Fe^{II} is virtually unlimited compared to Fe^{III}, this process can help solubilize Fe on sinking dust and detrital particles.

As is now well known, marine sediment core records show that during glacial periods dust deposition to the ocean increased by 2- to 20-fold over current interglacial fluxes (Lambert *et al.*, 2008). Correlations between Fe and biogenic silica within sediments suggest that the increased iron contributed to increases in diatom productivity during past glacial maximum periods. The resultant release of iron stress in the ocean may have a) permitted phytoplankton in HNLC regions to deplete a greater portion of the surface nutrients (and more effectively pump C into the ocean interior), b) stimulated the pumping of carbon to greater depths in the ocean via stimulating diatoms relative to other plankton, and c) stimulated the growth of diazotrophs, thus relieving the ocean of its nitrogen deficiency relative to phosphate (Moore *et al.*, 2006). Modeling studies indicate that together these factors could have contributed substantially to the drawdown in CO₂ during glacial maxima. Such effects of Fe would have been amplified if the increases in ocean phosphate indicated from

recent studies of marine sediment cores occurred as well (Filippelli *et al.*, 2007).

Ocean iron fertilization in HNLC regions, as tested to date, exhibits important similarities and differences from natural inputs of iron to the ocean. The first difference is that during OIF, iron is added to the water as Fe^{II} rather than Fe^{III}-oxides. However, the added Fe^{II} oxidizes to Fe^{III} in a matter of minutes and concentrations in excess of the 0.5-1 nM bound by natural ligands will precipitate as amorphous Fe^{III}-oxides. Thus, although not identical to a dust addition, the difference lies mostly in very short-term reactions and possibly in the fraction that remains dissolved. A second difference lies in the geographical locations. OIFs are planned for areas where dust inputs to the ocean are minimal during interglacial periods. Thus, the iron cycle will be significantly augmented there relative to its current functioning, although perhaps not compared to the iron cycle during glacial maximum conditions where large inputs to HNLC regions have occurred.

Use of Conceptual Model in the Master Environmental Report

The Conceptual Model will be used in preparation of a Master Environmental Report (MER) by providing a description of the biogeochemical cycles occurring in the ocean and an understanding of how OIF works. The MER will include a description of the design of the planned project and the expected benefits. The major components of the MER are listed in Table 2.

Table 2
Contents of the MER

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| <p>Summary of Planned Project</p> <ul style="list-style-type: none"> • Overview of OIF • Description of Project Design • Criteria for Site Selection • Potential Benefits of Project • Potential Effects of Project <ul style="list-style-type: none"> – Local Marine Biota – Higher Trophic Levels – Ocean Chemistry – Greenhouse Gases – Other Gases • Summary of Issues and Responses • Monitoring Procedures • Mitigation Measures • References |
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In responding to the potential benefits and effects of the project, the conceptual model will address the primary questions that have been raised regarding the effectiveness

of OIF as a sequestration technique and potential ecological effects of stimulating primary production in marine waters. A list of these primary questions is presented in Table 3.

Table 3
Primary Environmental Concerns
Addressed in the Ocean Iron Fertilization Conceptual Model

The oceans are a major source of the world's oxygen and sink for atmospheric CO₂. Anything that may affect the associated processes is an environmental concern. The OIF Conceptual Model will identify these concerns raised by various groups and how they can be addressed through field monitoring and contingencies incorporated into the experiment design.

Remineralization	A fraction of the carbon fixed as algal biomass, fecal pellets, etc., may be mineralized well before settling to become a portion of deep storage or loss to sediments. A variable portion of the fixed carbon thus may not be sequestered.
Permanent Sequestration	Measurements needed to show that OIF is effective and that carbon is sequestered to depths of about 400 m; OIF experiments typically did not measure POC fluxes at depth for >30 days.
Less Primary Production	Self-shading and/or cooling due to increased productivity may affect deeper ocean water column.
OIF's Effectiveness	OIF's contribution to reduction of CO ₂ in atmosphere is uncertain; efficacy may be relevant in light of potential adverse environmental impacts. Measurements of air-sea flux are needed to show drawdown of CO ₂ in air.
Purity and Fate of Iron	Source of iron used for OIF may introduce other trace metals as impurities, which could have toxic effects on water column biota. Also need to show the fate of added iron, particularly how much reaches the lower water column and potential effects on benthic organisms.
Hypoxia/Anoxia	Detrital material resulting from phytoplankton growth and settling may exert a demand on ocean oxygen resources as it decays.
Toxic Algae	Growth of toxic algae may occur during fertilization, e.g., dinoflagellates and some species of diatoms.
Formation of By-Products	Non CO ₂ greenhouse gases (e.g., N ₂ O, CH ₄) and other compounds (e.g., dimethyl sulfide) may be produced during or following OIF.
Downstream Nutrient Depletion	N and P removed by iron fertilization may not be available to support downstream (down current) food webs.
Food-Web Effects and Ecosystem Shifts	OIF may stimulate changes in types and relative amounts of plankton species, which could affect higher trophic levels including fish, birds, or mammals.
Biogeochemical Cycles	Sequestering of additional carbon may detrimentally affect the cycling of other oceanic elements and compounds such as silica.
Other Chemical and Physical Effects	OIF may lead to increased ocean acidification or to changes in the natural SST and surface heat fluxes. OIF could contribute to eutrophication.
Other Biological Effects	OIF could possibly lead to interference with breeding or migration patterns, particularly for sensitive species.

Preparation of the Conceptual Model and Master Environmental Report

The OIF Conceptual Model and Master Environmental Report will be developed by Tetra Tech's Research & Development Group in Lafayette, California. Tetra Tech is a leading multinational consulting and engineering firm with extensive expertise in environmental impact analysis. Tetra Tech's R&D Group has specialized experience in biogeochemistry, carbon cycling and coupled global climate modeling as well as expertise in developing thorough environmental impact reports for a wide range of projects. The team has previously been recognized for its significant scientific contributions and the ability to effectively communicate study results to a wide audience of interested parties and decision makers. Tetra Tech's report on mercury biogeochemical cycling in lakes (Hudson et al., 1994) provides a good example of the technical approach applied in developing this type of conceptual model. An example of a conceptual model developed to explore and explain the behavior of metals in the estuarine environment is available at: <http://www.sanjoseca.gov/esd/PDFs/CMR-Cvr-Sec-3.pdf>

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