Modeling the geochemical cycle of iron in the oceans and its impact on atmospheric CO_2 concentrations

Nathalie Lefèvre[1] and Andrew J. Watson

School of Environmental Sciences, University of East Anglia, England, United Kingdom

Abstract. Iron occurs at very low concentrations in seawater and seems to be a limiting factor for primary production in the equatorial Pacific and the Southern Ocean. The global distribution of iron is still not well understood because of a lack of data and the complex chemistry of iron. We develop a 10-box model to study the oceanic distribution of iron and its effect on atmospheric CO_2 concentration. Subject to our assumptions, we find that a lack of interocean fractionation of deep sea iron concentrations, as suggested by *Johnson et al.* [1997a], is not readily explained by a balance of eolian deposition, scavenging, and regeneration. Incorporation of organic complexation in the model, as suggested by Johnson et al., to reduce the scavenging rate of iron when concentrations fall below some ligand-stabilized concentration, is one solution to this difficulty. Alternatively, the deep-sea concentration may be more variable than the current, rather sparse data coverage suggests. In the model, deep-sea iron concentrations are responsive to the atmospheric source, even if we adopt stabilization of concentrations by a ligand as modeled by *Johnson et al.* [1997a]. In the Southern Ocean, where the model suggests iron supply has an important limiting effect on the biota, more than 99% of the iron supply to the surface in the present day comes from upwelling and not from the local atmospheric flux. In the context of glacial-interglacial changes to atmospheric CO_2 the model suggests that increasing atmospheric iron to the entire global ocean by a factor of 2, leads to decreases in atmospheric CO_2 of 10-30 ppm, depending on assumptions. However, in our model, CO_2 concentrations are almost unaffected by changes in Southern Ocean atmospheric fluxes alone, unless these are unrealistically large (>100 times present day). The effect on atmospheric carbon dioxide is slightly stronger if accompanied by increased stratification of the Southern Ocean. The model suggests that eolian "iron fertilization" of the ocean could have importantly influenced glacial atmospheric CO_2 concentrations but that other processes must also be at work to account for the full magnitude of the glacial-interglacial change.

1. Introduction

In the Southern Ocean, the subarctic Pacific, and the equatorial Pacific, the supply and assimilation of the macronutrients nitrate and phosphate are not tightly coupled and the biological pump seems inefficient. These regions exhibit "high-nutrient low-chlorophyll" (HNLC) waters, and many hypotheses have been proposed to account for them: The phytoplankton growth may be limited by zooplankton grazing [*Walsh*, 1976; *Minas and Minas*, 1992], light limitation (especially in the Southern Ocean [*Priddle et al.*, 1986]), or the availability of iron [*Martin and Fitzwater*, 1988 ; *Martin et al.*, 1990a, b]. Laboratory experiments and in vitro enrichments have shown that iron does affect phytoplankton growth. Recently, an in situ iron fertilization experiment has shown that enhanced productivity was associated with increased iron concentrations in the equatorial Pacific [*Martin et al.*, 1994]. In a second such experiment, iron fertilization led to a massive diatom bloom [*Coale et al.*, 1996; *Frost*, 1996; *Behrenfeld et al.*, 1996] resulting in a large decrease of oceanic pCO_2 [*Cooper et al.*, 1996].

If there is now strong evidence of the role of iron in phytoplankton growth, little is known about the distribution of iron in the world ocean and the processes governing its distribution. There is a lack of data because of the difficulty of measuring iron concentrations accurately. Recently, *Johnson et al.* [1997a] published the largest data set so far available for iron in different regions. They observe that iron behaves like other nutrients, in that it exhibits strong depletion due to biological uptake in surface waters, while the concentration increases with depth because of the remineralization of the settling particles. However, in contrast with other nutrients, the deep water concentration of iron seems to be nearly constant in the different ocean basins. They explain this constancy in deep waters by complexation with an organic ligand, the concentration of which might set the mean ocean deep water iron concentration. *Boyle* [1997] argues against the control of iron concentration in deep waters by a ligand

---

[1] Also at Plymouth Marine Laboratory, Plymouth, England, United Kingdom.

and defends *Bruland et al.*'s [1994] idea that the balance of eolian supply, regeneration, and scavenging may explain the iron distribution.

Here we use a simple reservoir-flux model of the global ocean to better understand some aspects of the marine geochemistry of iron. Such "box" models have the advantage of being simple and computationally efficient. While the spatial resolution of a box model is poor, it is perhaps appropriate, given the very limited amount of data so far available for iron. A 10-box model has been used to reproduce the iron distribution for the world ocean, to examine the consistency of simple chemical schemes with the available data, and to make predictions about the effect of changing the iron supply on ocean productivity. The impact of eolian iron deposition on atmospheric CO_2 is also tested to address the "iron hypothesis" as a mechanism for causing the glacial to interglacial changes observed in ice core records, there being evidence of greater atmospheric deposition of windblown dust during glacial time [*De Angelis et al.*, 1987; *Petit et al.*, 1990, *Mahowald et al.*, 1999].

2. Description of the Model

We desired to model explicitly the possibly iron-limited regions of the North Pacific and Southern Oceans and to investigate interocean fractionation of iron between the deep Atlantic, Pacific, and Antarctic oceans. We chose PANDORA, the 10-box model of *Broecker and Peng* [1986, 1987, 1989] because, while otherwise simple, it resolves these regions. Figure 1 shows the structure of the model with the flow patterns and the particulate fluxes of organic carbon. The magnitude of the water fluxes was chosen to yield the observed ^{14}C distribution in the ocean [*Broecker and Peng*, 1987]. The model was adapted to determine the steady state concentrations of phosphate (PO_4), total inorganic carbon (ΣCO_2), alkalinity (AT), and iron (Fe). Phosphate was used as the controlling macronutrient, as in the work of *Broecker and Peng* [1987]. For the processes considered here we assumed

constant C:N:P Redfield ratios, so nitrate could equally have been used. Water and particle fluxes, PO_4, ΣCO_2, and AT data were taken from *Broecker and Peng* [1987]. A "standard" iron distribution was deduced from data in the literature. The concentrations adopted are given in Table 1.

The spatial distribution iron that we adopt owes much to the compilation of *Johnson et al.* [1997a]. However, the paucity of iron data and the variability in some regions mean that considerable uncertainty is attached to some of the concentrations. For example, there is almost no data in the south central Pacific or Indian Oceans. Lacking this, we took the values given by Johnson et al. for the North and equatorial Pacific to be representative of the entire Indo-Pacific. In the surface North Atlantic, *Johnson et al.* report low rates, 0.1-0.3 nM. However, in the surface South Atlantic, *Bowie et al.* [1998] found dissolved iron levels ranging from 0.1 to 4.5 nM while *Powell et al.* [1995] measured total dissolved iron concentrations from 0.5 to 10 nM, with the higher values being associated with eolian inputs. Our value of 1.0 nM for the entire surface Atlantic is therefore subject to wide uncertainty. We could find no published data relating to deep-sea concentrations in the South Atlantic, so concentrations for the Atlantic deep water reservoir were taken from Johnson et al.'s measurements in the North Atlantic. It is apparent from this discussion that the overall picture given by the data of *Johnson et al.* [1997a], and generally adopted here, of little difference between deep Atlantic and Pacific concentrations of iron is very provisional. It could change substantially if the deep South Atlantic proves to have high Fe concentrations while the deep South Pacific is found to have low values [*Boyle*, 1997].

To incorporate a rudimentary geochemistry for iron in the model, we made additions to it as described below.

2.1. Atmospheric Input of Iron

We assumed that the supply of iron to the open ocean comes ultimately from eolian deposition, this input being
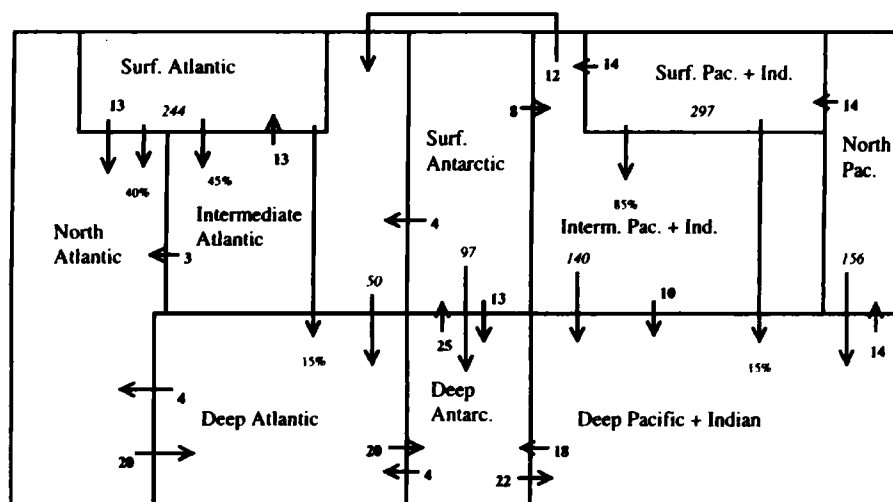

Figure 1. Structure of the 10-box model with water fluxes in sverdrups (plain arrows, figures in bold) and carbon organic fluxes in 10^4 mol C s^{-1} (dashed lines, figures in italic). The percentages correspond to the fraction of remineralization.

Table 1. Concentrations of PO_4, ΣCO_2, AT, and Iron for Each Box of the Model

Box	Ocean	PO_4, μmol kg^{-1}	ΣCO_2, mmol kg^{-1}	AT, meq kg^{-1}	Fe, μmol kg^{-1}
1	Surface Antarctic	1.71	2.200	2.371	0.07[a]
2	Surface Atlantic	0.04	1.931	2.255	1.0[b]
3	Surface Pacific	0.03	1.977	2.313	0.2[c]
4	North Atlantic	0.90	2.076	2.274	1.0
5	North Pacific	1.66	2.165	2.372	0.4
6	Intermediate Atlantic	1.48	2.169	2.316	0.76[c]
7	Intermediate Pacific	1.03	2.109	2.312	0.2[d]
8	Deep Antarctic	2.00	2.276	2.397	0.6[c]
9	Deep Atlantic	1.36	2.168	2.337	0.6[c]
10	Deep Pacific	2.52	2.332	2.447	0.6[c]

PO_4, ΣCO_2, AT data are from *Broecker and Peng* [1987] with concentrations in the intermediate boxes calculated from a budget at the steady state. AT is alkalinity.

[a] *De Baar et al.* [1995].

[b] *Bowie et al.* [1998].

[c] *Johnson et al.* [1997a].

[d] *Martin and Fitzwater* [1988].

balanced at steady state by the loss to sediments. For the Atlantic Ocean, there is a large supply of dust from the Sahara whereas, the supply to the most of the Pacific and the Southern Oceans is low [*Duce and Tindale*, 1991; *Mahowald et al.*, 1999]. Atmospheric inputs of iron are thought to play an important role in local *productivity [Young et al.*, 1991; *Moore et al.*, 1984] and have been suggested as the major supply of iron to the remote ocean [*Duce and Tindale*, 1991]. Data from *Duce et al.* [1991] were used to estimate the atmospheric input of iron in the surface waters (surface Antarctic, surface Atlantic, surface Pacific, North Atlantic, North Pacific, intermediate Atlantic, and intermediate Pacific). According to *Duce and Tindale* [1991], between 10 and 50% of the total atmospheric Fe entering the world ocean appears to dissolve. However, recent estimates suggest that the true figure might be considerably less than 10%, perhaps only 2% [*Jickells and Spokes*, 1999]. We assumed a solubility of 10% for iron in dust as our standard case (*Moore et al.*, 1984, *Duce et al.*, 1991) but also examined the effect of assuming lower solubility. If the solubility of iron in dust is 10%, the total atmospheric flux of iron to the ocean is 3.2×10^{12} g yr^{-1} on Duce et al.'s figures. We made estimates of

the iron flux as dust received by each region using the map published by *Duce et al.* [1991], so that an iron flux could be determined for each surface box (Table 2).

The importance of atmospheric iron supply as a control of deep iron concentrations is a subject of controversy. *Johnson et al.* [1997a] argued against the role of atmospheric dust as the dominant control on the iron supply to the deep ocean because they could not find a correlation between the 0-500 m inventory of Fe and the estimated eolian iron flux for their stations. *Boyle* [1997] suggested that a station-by-station comparison of the local dust flux with water column iron is misleading because the estimated residence time of iron (100-200 years) allows significant lateral transport. In subsequent comment, *Johnson et al.* [1997b] show some data from the Pacific where there does appear to be some correlation between atmospheric supply and concentrations in the top 500 m.

2.2. Iron Transport, Uptake, and Regeneration

In the model, iron is incorporated into particles by photosynthesis (in surface waters) and scavenging (in all reservoirs) and returned to the dissolved phase by particle remineralization. The complete equation for Fe concentration in a given box j is given by

$$V_j \frac{\partial [Fe]_j}{\partial t} = \sum_{i \neq j} \left\{ f_{ij}[Fe]_i - f_{ji}[Fe]_j + g_{ij}(Fp_iR_i + S_i) \right\}$$

$$-Fp_j R_j - S_j + F_{j(atm)}, \qquad (1)$$

where V_j is the volume of the box j, f_{ij} is the water flux from box i to box j, $F_{j(atm)}$ is the flux into box j from the atmosphere (zero if the reservoir is not at the surface), Fp_i is the flux of particles (in moles of carbon per unit time) generated in box i, R_i is the Fe:C molar ratio with which these particles were formed (i.e. excluding effects of scavenging), g_{ij} is the fraction of particles from box i which remineralize in box j, and S_i is the flux of iron scavenged onto the particles in box i. Both f_{ij} and g_{ij} are, of course, normally zero for nonadjacent reservoirs.

Table 2. Atmospheric Flux of Iron to the Different Surface Boxes of the Model and the Corresponding Percentage of the Total Flux

	Surface Boxes	Flux of Iron, nmol cm^{-2} yr^{-1}	% of total flux
1	Surface Antarctic	0.02	0.1
2	Surface Atlantic	6.76	41.3
3	Surface Pacific	0.67	4.1
4	North Atlantic	0.13	0.8
5	North Pacific	1.35	8.3
6	Intermediate Atlantic	6.76	41.3
7	Intermediate Pacific	0.67	4.1

Figures are based on the assumption of dust input map of *Duce et al.* [1991], 3.5%w/w content of iron, and 10% solubility of this iron.

The left-hand side of this equation is the rate of change of the total amount of iron in each reservoir, and the right-hand side is the algebraic sum of dissolved and particulate iron fluxes, the fluxes due to iron incorporation during net photosynthesis being treated separately from those due to scavenging. Following the approach of *Johnson et al.* [1997a], we assumed a constant lifetime everywhere in the ocean against scavenging. Initially, this term was calculated as

$$S_i = V_i k[Fe]_i, \qquad (2)$$

where k is the rate of scavenging ($1/k$ is the lifetime against scavenging).

Consistent rates of particle formation, as fluxes of carbon, are specified for PANDORA by *Broecker and Peng*, [1987], as are the rates of remineralization, g_{ij}. These can be converted to the iron fluxes if C:Fe "Redfield" ratios for carbon to iron can be specified in the particles. However, unlike the classical Redfield ratios C:N:P, the C:Fe ratio seems to be highly variable and depends on the availability of iron. *Sunda* [1997] has reviewed the evidence for variable C:Fe ratios in the world ocean: Experiments with cultures of oceanic phytoplankton show that the proportion of Fe to C in cells increases with increasing external iron. Correspondingly lower rates of iron regeneration relative to consumption of O_2 with depth are found in iron-limited regions such as the Pacific and Southern Oceans. Higher Fe:C (lower C:Fe) ratios are then expected in waters containing higher available iron concentrations.

Using the PANDORA model at steady state, "geochemical" particulate C:Fe ratios may be calculated by equating the right hand side of (1) to zero in each reservoir. This can be solved for each R_j if the dissolved concentrations in each box are specified and by taking the particulate carbon fluxes and remineralizations (Fp_j and g_{ij}) from the work of Broecker and Peng [1987]. By this means, the values that the iron "Redfield ratio" must adopt in each box to be consistent with the assumed dissolved iron concentrations, atmospheric fluxes, and scavenging rates can be obtained. Adoption of this set of values for the Redfield ratios is a necessary, but not a sufficient, condition for the steady state of the model to reproduce the assumed iron distribution.

To be physically realistic, the downward iron flux carried by particles out of each reservoir (equal to ($FpR_j + S_j$) in (1)) must be positive, but for arbitrary dissolved iron concentrations and dust input, this net flux might equally be negative. Thus not all combinations of eolian input are compatible with the "standard" iron distribution and other assumptions we made. This constraint produced occasional conflicts in our assumptions, discussed below in the context in which they occurred.

Initially, we ran the model to steady state, with the C:Fe ratios calculated as above, to be consistent with the "standard" iron distribution (Table 1), fluxes (Table 2), and scavenging rates adopted. Final distributions similar to the standard distribution then indicated a consistent set of assumptions.

In the model all the iron incorporated into particles by either photosynthesis or scavenging in the surface or intermediate reservoirs must return to the dissolved phase in another reservoir, for particulate material from the upper

boxes is entirely recycled within the ocean in PANDORA as set up by *Broecker and Peng* [1987]. However, iron scavenged onto particles in the deep reservoirs is not returned to solution but represents the net output from the ocean in this model. The atmospheric flux is the net input, so it is a condition of a consistent steady state solution that the total deep-scavenged flux must balance the total atmospheric flux.

For situations in which the model was forced a long way from the present-day steady state, as in the glacial-interglacial calculations presented in section 4, we modeled C:Fe ratios as a power-law dependency on iron concentrations

$$C:Fe \propto [Fe]^n,$$

where n was determined by fitting to the data of *Sunda and Huntsman* [1995] to be 0.45.

3. Modern-Day Distribution of Iron

3.1. The Eolian / Scavenging / Regeneration Scenario

We first tested the suggestion by *Boyle* [1997] and earlier by *Bruland et al.* [1994] that observed iron concentrations might be due to a balance between eolian input, scavenging and regeneration without the necessity to appeal to organic complexation. *Whitfield and Turner* [1987] classified trace metals according to their oceanic profiles as either nutrient-type or scavenged-type. Nutrient-type metals are removed from surface waters because of the biological uptake and then remineralized in deep waters. Their concentrations in the deep Atlantic Ocean are lower than in the older deep Pacific. In contrast, scavenged-type metals are removed even in deep waters, and their concentration maxima correspond to their external sources. They usually exhibit higher concentrations in the younger waters of the deep North Atlantic Ocean. Iron might then exhibit a mixture of these characteristic behaviors of nutrient-type and scavenged-type metals because it is both essential for phytoplankton and also strongly scavenged, these processes tending to compensate in such a way that there is no marked interocean fractionation.

For various values of scavenging rate in (2), the values of C:Fe ratio which were consistent with the standard iron distribution at steady state were determined, and the model was then run to steady state with these values. Initially, the incoming atmospheric iron solubility was fixed at 10%. The resulting iron distributions were compared with the standard iron distribution to examine the self-consistency of the asssumptions. Resulting iron concentrations and C:Fe ratios for our standard atmospheric input, and scavenging rates of 0.001 yr^{-1} and 0.002 yr^{-1} are shown in Figure 2. If the scavenging rate was larger, the eolian iron input became too small to balance scavenging losses, and the particle flux became negative. For the North Pacific Ocean, even a scavenging rate of 0.001 yr^{-1} was too fast, resulting in the model predicting a negative particle flux of iron. This indicates an inconsistency in the model assumptions for this region; either the atmospheric flux is too low or the transport of dissolved iron into the region is insufficient. We fixed the C:Fe ratio in this region at 2 x 10^5, which is equivalent to requiring a larger atmospheric Fe flux to the reservoir of about 6.6 nmol cm^{-2} yr^{-1} rather than the value from *Duce and*

Tindale [1991] of 1.4 nmol m^{-2} yr^{-1}. Another possible resolution of this inconsistency would involve reducing the productivity of this reservoir by a similar factor.

With scavenging rates of k = 0.002 yr^{-1} the iron concentration in surface waters is not too dissimilar from the standard case except, as discussed above, for the North Pacific (Figure 2). However, the concentration of iron in deep waters is similar to a scavenged-type distribution with highest concentrations observed near the main sources, that is, the Atlantic Ocean in the case of iron. When the scavenging rate is slower, the concentrations in the deep waters, particularly the Atlantic, become much higher than observed. The order of the deep ocean concentrations, Atlantic > Pacific > Southern Ocean, is the same as that of the atmospheric inputs, suggesting control of the deep iron distribution by eolian flux. Thus with simple first-order scavenging, and subject to our assumptions, we cannot reconcile a deep water distribution, which is relatively constant and rather low, with the distribution of eolian sources. If the scavenging rate is made faster, too much iron is scavenged in the oceans to match the atmospheric input, whereas if it is slower, the predicted deep water concentrations are too high.

As expected, the lowest C:Fe ratios correspond to the regions of the world ocean with highest iron supply (Figure 2). When the scavenging rate is slow (k = 0.001 yr^{-1}), there is more iron in the system and the C:Fe ratios are lower than those obtained with a faster scavenging rate.

As mentioned above, recent estimates of the solubility of iron in aerosol suggest that it may be much lower than 10% [*Jickells and Spokes*, 1999]. If the atmospheric input is reduced in the model by assuming a lower solubility, it is necessary to decrease the scavenging rate in order to obtain reasonably realistic concentrations of iron. Such a scenario also tends to reduce the dominance of the atmospheric imprint on deep-sea iron concentrations and so tends to improve the fit of the model steady state distribution to the observations. In Figure 2, therefore, we have also included the results of a

run where the atmospheric input was assumed to be only 2% soluble and scavenging rate was reduced to 5 x 10^{-4} yr^{-1}. This combination of factors reduces the difference in deep water concentrations between Atlantic and Pacific to about 50% of the concentrations. The concentrations are somewhat too high. However, the 2000 year lifetime for dissolved Fe in the deep sea is much longer than normally accepted. *Bruland et al.* [1994] estimate lifetimes of the order of 70-100 years on the basis of the assumption of equilibration with particulate iron and the residence time of particles in the deep sea. The observations of elevated iron concentrations near continental margins, dropping off rapidly with distance from land, also seem inconsistent with such a long residence time [*Boyle*, 1997].

We also considered whether the standard eolian flux we assumed might be too low, resulting in estimates of scavenging rates that are too low at steady state. The net input to the model would have to be increased by a factor of 3-10 to produce residence times of the order of Bruland *et al.*'s [1994] estimate, compatible with average concentrations in the deep sea similar to those observed. However, these assumptions lead to deep sea concentrations which bear a strong atmospheric imprint; that is, they are much higher in the Atlantic than in the Pacific.

3.2. Scavenging by a Ligand

Johnson et al. [1997a] hypothesized control of iron in deep waters by an organic ligand which reduces the scavenging rate of dissolved iron at concentrations less than about 0.6 nM. Evidence for such ligands has been found at concentrations of the right order, but very little is known about their chemical nature, lifetime, or origin [*Rue and Bruland*, 1995; *Van den Berg*, 1995; *Wu and Luther*, 1995; *Luther and Wu*, 1997]. We used our model to test this mechanism, with the scavenging function defined by *Johnson et al.* [1997a],

Figure 2. C:Fe ratios (mol μmol^{-1}) and iron concentrations (nmol kg^{-1}) determined at steady state for the eolian, scavenging, regeneration scenario with a scavenging rate k = 0.001 yr^{-1} (in italic), with a scavenging rate k = 0.002 yr^{-1} (in bold), and with a solubility of 2% and a scavenging rate k = 0.0005 yr^{-1} (underlined).

$$R_{fe} = k([Fe] - Fe_{sol}),$$

being introduced in each box. Here Fe_{sol} is the value of the effective solubility of iron as stabilized by the ligand, taken to be 0.6 nM.

As might be expected, inclusion of this scheme with a ligand and an otherwise high rate of scavenging, k=0.01 yr^{-1}, leads to a better reproduction of the standard iron profile (Figure 3). Concentrations in the deep Antarctic and deep Pacific are very similar and about 0.6 nM but still with a slightly higher concentration in the deep Atlantic. If the scavenging rate is slower ($k = 0.002$ yr^{-1}), the deep-sea concentrations, particularly in the Atlantic, become substantially higher than those observed.

To summarize this section, subject to our assumptions, we were unable to find a distribution yielding concentrations ~0.6 nM uniformly in the Atlantic and Pacific basins by adopting a constant rate of scavenging of iron; regeneration does not appear to balance the eolian input closely enough to eliminate concentration gradients in the deep ocean of the order of a factor of 2. One possibility is that such gradients do exist, in particular, between the central and South Atlantic and the South Pacific, and the data coverage is simply too sparse at present to show the full variability. Another possibility is that the lifetime of iron is much longer in the deep sea than previously supposed and that the net eolian input is considerably lower. On the other hand, we confirm that adopting *Johnson et al.*'s [1997] "ligand hypothesis" can help resolve this issue, but at the cost of proposing a ligand or ligands with nearly constant concentration in the deep sea. Presumably, any such ligand would have to be produced and consumed throughout the water column, probably by bacterial action. Alternatively, if it is produced at the surface by the ecosystem there, it would have to be transported efficiently to depth, or else have an extremely long lifetime, in order to be so uniformly distributed. In section 4, we tentatively adopt the Johnson et al. model, in which deep sea concentrations are stabilized by a ligand, with a scavenging rate of 0.01 yr^{-1}, as we continue our investigation into the impact of changing eolian iron supply on atmospheric CO$_2$.

4. Glacial–Interglacial Changes in Iron and CO$_2$

Martin et al. [1990a, b] suggested that increased atmospheric input of iron to the Southern Ocean during glacial times could be responsible for higher productivity and hence lower atmospheric pCO$_2$. Productivity in this region has been observed to differ with iron abundance in the water [*De Baar et al.*, 1995]. Though we do not have strong evidence in favor of the Johnson ligand hypothesis, we expect iron concentrations in the sea will be less responsive to changes in the eolian flux in this scenario than in those in which no ligand is included; thus our assumptions are conservative, in the sense that our choice of iron chemistry will not cause us to overestimate the possible changes.

Previous authors have shown the importance of high latitude regions in setting the atmospheric pCO$_2$ [*Sarmiento and Toggweiler*, 1984; *Knox and McElroy*, 1984; *Wenk and Siegenthaler*, 1985]. The atmospheric input of iron is the lowest for the Southern Ocean. The flux of iron deduced from the map of *Duce et al.* [1991] is 0.02 nmol cm^{-2} yr^{-1} (Table 2). The other supply of iron to the surface Antarctic reservoir comes from the water flux (25 Sv) between the surface and the deep Antarctic (Figure 1). From these figures it appears that today about 99% of the iron supply to the surface of the Southern Ocean comes from the upwelling, a conclusion which would be reinforced if our assumed solubility of atmospheric dust is too high.

The reasons for the shift between atmospheric pCO$_2$ in glacial time (200 µatm) and interglacial times (280 µatm) are not well understood, and changes of oceanic circulation [*Keigwin et al.*, 1991, 1994; *Broecker*, 1997; *Ganopolski et al.*, 1998] or biological productivity [*Murray et al.*, 1993; *Kumar et al.*, 1995] have all been advanced as possible explanations. There is evidence of increased atmospheric dust by a factor of 10-50 [*De Angelis et al.*, 1987; *Petit et al.*, 1990] which must have increased the iron supply to the ocean. Recent simulation of glacial climate confirms the strengthening of the winds [*Ganopolski et al.*, 1998], while *Murray et al.* [1995] found that in glacial time the flux of terrigenous Fe was several orders of magnitude larger than

Figure 3. C:Fe ratios (mol µmol^{-1}) and iron concentrations (nmol kg^{-1}) determined at steady state with a scavenging rate k = 0.01 yr^{-1} (in bold) and k = 0.002 yr^{-1} (in italic) by a ligand.

modern observations of eolian Fe input in the equatorial Pacific.

In order to investigate the role of changing iron concentrations, we first had to consider whether there were other changes in the model which would be appropriate to glacial time. We considered changes in temperature, salinity, nutrients, carbon parameters, and circulation as follows.

4.1. Glacial Ocean Chemistry

Broecker [1982] and *Ganeshram et al.* [1995] suggested large changes in oceanic nutrient inventories during glacial time, whereas *Boyle* [1988] proposed a transfer of nutrients from intermediate waters into deeper waters without changes in the inventory, which requires an increase of alkalinity. The increase in salinity [*Broecker*, 1982] due to storage of fresh water in ice caps affects both the alkalinity and the total carbon inventory by about 3%. There is also believed to have been a 1.4% higher carbon inventory in the oceans during glacial time [*Broecker and Peng*, 1993], estimated from a change in ^{13}C, because of the growth of the forest and soil organic reservoirs during early interglacial time. Carbon and alkalinity changes may also have been affected by massive coral growth during the rise in sea level.

We adopted a "glacial ocean chemistry" as follows. Compared to the modern ocean, the average temperature in the model was 2°C cooler, the mean salinity increased by 0.9 unit, the mean ΣCO_2 was 4.3% higher, and the mean alkalinity was 5% higher. With all these changes the steady-stated atmospheric $p CO_2$ dropped from 278 to 252 μatm, when other conditions were left the same.

4.2. Glacial Ocean Circulation

A slower "conveyor belt" circulation is frequently postulated for glacial time, but there is no general agreement on this subject. The effect of changes in thermohaline circulation has been investigated by other authors [i.e., *Sarmiento and Toggweiler*, 1984, *Siegenthaler and Wenk*, 1984]. Recent work seems to argue against the idea of large changes in the thermohaline circulation. For example, *Yu et al.* [1996] infer similar rates of total North Atlantic deep water formation from radiochemical data, while a recent simulation of a glacial climate in a global coupled ocean-atmosphere model [*Ganopolski et al.*, 1998] also suggests only a slight reduction of the rate of North Atlantic Deep Water formation. As there are a large number of ways, even in our simple model, in which such a change could be modeled, we chose not to vary this aspect of the circulation from that of the modern day.

François et al. [1997] have recently presented new evidence supporting an increased surface-water stratification in the Southern Ocean. Increased Southern Ocean stratification can be comparatively easily modeled in PANDORA without changing anything else by decreasing the rate of exchange between surface and deep Southern Ocean reservoirs. The maximum reduction of the upwelling, which corresponds to a shutdown of the downwelling, is about a factor of 2 (25-12 Sv). A further reduction of the upwelling rate would involve other modifications of the circulation.

4.3. Effect of Iron Limitation

Biological activity is limited by the amount of macronutrients (phosphate, in this model) and iron available in the surface waters. An increase of the productivity should correspond to a stronger export of carbon to the deep ocean and would also affect the C:Fe ratio. In order to take into account this process the C:Fe ratio in surface waters (surface Antarctic, Atlantic, and Pacific) was linked to the iron concentration according to the power law deduced from the data of *Sunda and Huntsman* [1995]. The particle flux was linked to the phosphate and iron concentrations using a Michaelis-Menten formulation:

$$F_p = F_{max} \frac{[PO_4]}{[PO_4]+[PO_4]_0} \frac{[Fe]}{[Fe]+[Fe]_0}, \qquad (3)$$

where $[PO_4]_0 = 0.03$ μmol kg^{-1}.

It is far from clear how to choose a representative value for $[Fe]_0$, the concentration at which growth rate is half its maximum. Measurements of the response to iron limitation by different species of phytoplankton show that iron requirements differ substantially between species, with oceanic species typically having much lower requirements than coastal varieties [*Sunda et al.*, 1991]. For oceanic species such as the coccolithophore *Emiliania Huxleyi* and the diatom *Thalassiosira Oceanica*, measurements in culture suggest that true limitation does not set in until dissolved inorganic iron concentration [Fe'] is reduced to ~3 pM [*Sunda and Huntsman*, 1995]. However, because dissolved iron is found overwhelmingly in organically complexed form, the use of such a low concentration for $[Fe]_0$ in (3), which is written in terms of total dissolved iron, would be incorrect. The ligand concentrations and conditional stability constants observed in natural seawater by *Rue and Bruland* [1995], suggest that only ~3 x 10^{-4} of dissolved Fe(III) is in the inorganic form. Combining the above figures would indicate that $[Fe]_0$ may be ~10nM in the surface ocean. Such a high value would suggest that phytoplankton in iron-limited regions are growing at ~1% of their maximum growth rate at the ambient iron concentrations, which is too low to maintain a viable *population* [*Sunda and Huntsman*, 1995]. One possible explanation is that dissolved inorganic iron [Fe'] is maintained at higher-than-equilibrium values as a result of photochemical *processes* [*Johnson et al.*, 1994]. A lower limit on $[Fe]_0$ can be obtained from the empirical observation that for iron limitation in the HNLC regions to be important, the effective value of $[Fe]_0$ must be greater than the concentration in surface waters there. For the model we chose $[Fe]_0$ to be either 0.2 nM (a lower limit, we believe) or 1 nM, a more reasonable best estimate.

In the absence of perturbation (no change of productivity) the model was initialized to give the carbon fluxes of *Broecker and Peng* [1987] by adjusting the value of F_{max}, the maximum possible particle flux in (3). The value of F_{max} depends on the initial iron concentrations and the half-saturation constants for phosphate and iron. If $[Fe]_0$ is 0.2 nM, the maximum export production (calculated from (3) with initial iron and phosphate concentrations) is only three times Broecker and Peng's value, whereas it reaches 11 times when $[Fe]_0 = 1$ nM.
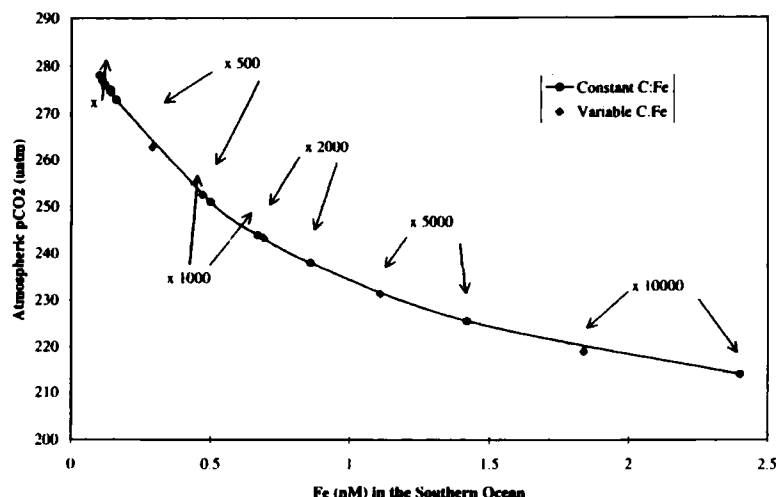
Figure 4. Evolution of pCO_2 in response to an increase of the atmospheric flux of iron in the Southern Ocean, for the present ocean, with $[Fe]_0 = 1$ nM, with variable C:Fe (diamonds) and constant C:Fe ratio (circles). The pCO_2 is plotted as a function of the iron concentration in the Southern Ocean. The data points correspond to the initial value, an atmospheric flux of iron multiplied by 20, 40, 60, 100, 500, 1000, 1500, 2000, 5000, and 10,000, respectively.

Runs to steady state with different atmospheric iron inputs, ocean chemistries, ocean circulations, and values of $[Fe]_0$ were made and are documented in Table 3 and Figures 4 and 5. In all cases, changing the atmospheric iron supply to the Southern Ocean by a factor of 20 (the magnitude of increase which might be expected in glacial time) has almost no effect on atmospheric CO_2. This is because the atmospheric flux of iron is two orders of magnitude lower than the water fluxes coming in the Antarctic box. A more significant input of atmospheric iron is necessary to increase the iron concentration in the Southern Ocean and hence decrease the phosphate concentration and the atmospheric pCO_2. On the other hand, a global increase of atmospheric iron by a factor of 2 is sufficient to decrease atmospheric pCO_2 by ~ 20 µatm, for the case $Fe_0 = 1$ nM. Increasing both the Southern Ocean input by 20 and the rest of the ocean input by a factor of 2 has an additive effect. For a given input of iron the magnitude of the decrease of pCO_2 is the same whether the "glacial" or

"modern" carbon and alkalinities are used, so subsequent runs (Figures 4 and 5) are presented only for the modern ocean.

Figure 4 shows in more detail the effects of increasing atmospheric Southern Ocean iron flux only and Figure 5 shows the effect of increasing the global flux of iron. Increasing the Southern Ocean flux only begins to have a pronounced effect if the increase is > 100 times the present day flux, which we take to be ruled out by the data. However, modest global increases have a very significant impact on the atmospheric concentration, an increase by a factor of 10 everywhere leading to a pCO_2 decrease about 50 µatm. Figure 5 also shows the influence of the variable, versus fixed, C:Fe ratio assumptions; within the range studied, there is little overall difference between the two. The difference is significant for large iron inputs only (Figure 4).

The effect of increasing stratification in the Southern Ocean by itself has, in this model at least, rather little effect, reducing atmospheric CO_2 by only 3 µatm (Table 3). This is

Table 3. Decrease of pCO_2 During Glacial and Interglacial Times for Different Ocean Circulations, Iron Inputs and Value of the Half Growth Constant $[Fe]_0$

Oceanic Circulation	Iron Input	pCO_2, µatm	
		$[Fe]_0=0.2$ nM	$[Fe]_0=1$ nM
	Modern Ocean Chemistry		
Modern	Standard	278	278
Modern	x 20 in the Southern Ocean	277 (-1)	277 (-1)
Modern	x 2 in all boxes	268 (-10)	255 (-23)
	Glacial Ocean Chemistry		
Modern	Standard	252	252
Modern	x 20 in the Southern Ocean	251 (-1)	251 (-1)
Modern	x 2 in all boxes	243 (-9)	232 (-20)
Reduced upwelling (12 Sv)	Standard	249	249
Reduced upwelling (12 Sv)	x 20 in the Southern Ocean	246 (-3)	246 (-3)
Reduced upwelling (12 Sv)	x 2 in all boxes	237 (-12)	225 (-24)

Figures in parentheses correspond to the change from the corresponding "standard" run.
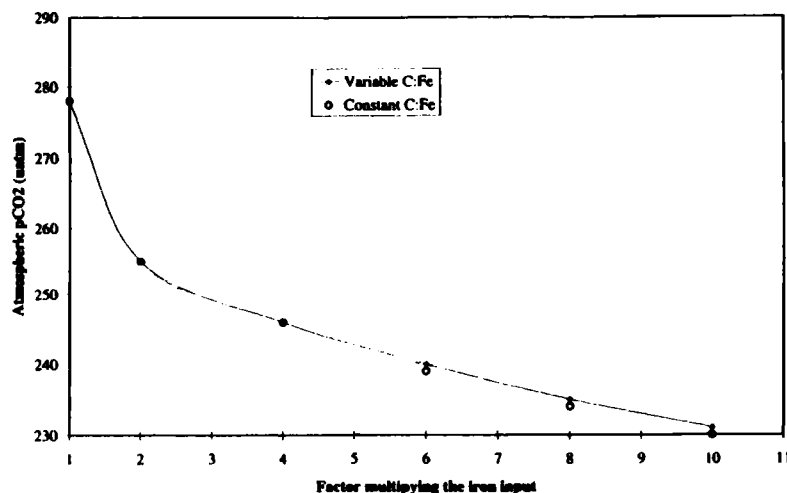
Figure 5. Evolution of $p\text{CO}_2$ in response to an increase of the atmospheric flux of iron everywhere, for the present ocean, with $[\text{Fe}]_0 = 1$ nM, with variable C:Fe (diamonds) and constant C:Fe (circles). Atmospheric $p\text{CO}_2$ is plotted as a function of the factor multiplying the atmospheric flux of iron.

because the region is kept in the HNLC condition by lack of iron, which is largely supplied by upwelling. Increasing the stratification does not therefore result in a greater efficiency of carbon uptake, because the iron supply is also restricted. However, if increased stratification is accompanied by higher iron flux from the atmosphere, this has a larger influence than either effect by itself. The model suggests that for the size of changes in atmospheric iron which are indicated by records of dust deposition in glacial time, decreases in atmospheric CO_2 of ~25 μatm might well be ascribed to effects of increased iron supply interacting with changes in Southern Ocean circulation. It does not seem possible to ascribe the ~80 μatm total glacial-interglacial change to changes in iron input to the oceans alone, however.

5. Conclusions

Previous studies of the effect of changes in iron supply on global atmospheric CO_2 have diagnosed upper limits on the effect by assuming that sufficient iron is added to the system to completely alleviate the "HNLC" status of critical regions such as the Southern Ocean [*Sarmiento and Orr*, 1991; *Peng and Broecker*, 1991]. The inclusion of a crude model for the biogeochemistry of iron allows us to refine these estimates somewhat. For example, *Sarmiento and Orr* [1991] calculate a maximum possible depression of atmospheric CO_2 of 72 μatm due to complete alleviation of Southern Ocean iron deficiency. Our model suggests an amplitude of ~25 μatm, making it an important but not dominant contributor to the overall glacial-interglacial CO_2 change. A decrease of 50 μatm might be reached if the atmospheric iron flux increased by a factor of 10 everywhere.

If we accept the figures of *Duce et al.* [1991] for atmospheric iron flux to the Southern Ocean and *Johnson et al.* [1997a] for deep water iron concentrations, it follows that in the Southern Ocean today, the main source of iron to the surface (~99%) comes from upwelling, the atmospheric flux of iron being very low. If the absence of substantial interocean fractionation of deep water iron concentrations is accepted, then our model suggests scavenging by a ligand is necessary to reproduce the observations. More data are

needed here, however, to shed further light on this question, since lack of interocean fractionation is not unequivocally established.

References

Behrenfeld, M.J., A.J. Bale, Z.S. Kolber, J. Aiken, and P.G. Falkowski, Confirmation of iron limitation of phytoplankton photosynthesis in the equatorial Pacific Ocean, *Nature, 383*, 508-511, 1996.

Bowie, A.R., E.P. Achterberg, R.F.C. Mantoura, and P.J. Worsfold, The determination of sub-nanomolar levels of iron in seawater using flow injection chemiluminescence detection, *Anal. Chim. Acta, 361*, 189-200, 1998.

Boyle, E.A., Vertical oceanic nutrient fractionation and glacial/interglacial CO_2 cycles, *Nature, 331*, 55-56, 1988.

Boyle, E.A., What controls dissolved iron concentrations in the world ocean? A comment, Mar. Chem., 57, 163-167, 1997.

Broecker, W.S., Glacial to interglacial changes in ocean chemistry, *Prog. Oceanogr., 11*, 151-197, 1982.

Broecker, W.S., Thermohaline circulation, the Achilles heel of our climate system: Will man-made CO_2 upset the current balance?, *Science, 278*, 1582-1588, 1997.

Broecker, W.S., and T.-H. Peng, Carbon cycle: 1985 glacial to interglacial changes in the operation of the global carbon cycle, *Radiocarbon, 28(2A)*, 309-327, 1986.

Broecker, W.S., and T.-H. Peng, The role of CaCO_3 compensation in the glacial to interglacial atmospheric CO_2 change, *Global Biogeochem. Cycles, 1*, 15-29, 1987.

Broecker, W.S., and T.-H. Peng, The cause of the glacial to interglacial atmospheric CO_2 change: A polar alkalinity hypothesis, *Global Biogeochem. Cycles, 3*, 215-239, 1989.

Broecker, W.S., and T.-H. Peng, What caused the glacial to interglacial CO_2 change?, *The Global Carbon Cycle*, , edited by M. Heimann, *NATO ASI Ser. I, 15*, 95-115, 1993.

Bruland, K., K.J. Orians, and J.P. Cowen, Reactive trace metals in the stratified central North Pacific, *Geochim. Cosmochim. Acta, 58*, 3171-3182, 1994.

Coale K.H., S.E. Fitzwater, R.M. Gordon, K.S. Johnson, and R.T. Barber, Control of community growth and export production by upwelled iron in the equatorial Pacific Ocean, *Nature, 379*, 621-624, 1996.

Cooper, D.J., A.J. Watson, and P.D. Nightingale, Large decrease in ocean-surface CO_2 fugacity in response to in situ iron fertilization, *Nature, 383*, 511-513, 1996.

De Angelis, M., N.I. Barkov, and V.N. Petrov, Aerosol concentrations over the last climatic cycle (160 kyr) from an Antarctic ice core, Nature, 325, 318-321, 1987.

De Baar, H.J.W., J.T.M. de Jong, D.C.E. Bakker, B.M. Löscher, C. Veth, U. Bathmann and V. Smetacek Importance of iron for plankton blooms and carbon dioxide drawdown in the Southern Ocean, Nature, 373, 412-415, 1995.

Duce, R.A., and N.W. Tindale, Atmospheric transport of iron and its deposition in the ocean, Limnol. Oceanogr., 36(8), 1715-1726, 1991.

Duce, R.A., et al., The atmospheric input of trace species to the world ocean, Global Biogeochem. Cycles, 5, 193-259, 1991.

François, R., M.A. Altabet, E.-F. Yu, D.M. Sigman, M.P. Bacon, M. Frank, G. Bohrmann, G. Bareille, and L. Labeyrie, Contribution of Southern Ocean surface-water stratification to low atmospheric CO$_2$ concentrations during the last glacial period, Nature, 389, 929-935, 1997.

Frost, B.W. Phytoplankton bloom on iron ratios, Nature, 383, 475-476, 1996.

Ganeshram, R.S., T.F. Pedersen, S.E. Calvert, and J.W. Murray, Large changes in oceanic nutrient inventories from glacial to interglacial periods, Nature, 376, 755-758, 1995.

Ganopolski, A., S. Rahmstorf, V. Petoukhov, and M. Claussen, Simulation of modern and glacial climates with a coupled global model of intermediate complexity, Nature, 391, 351-356, 1998.

Jickells, T.D., and L.J. Spokes, Atmospheric Input to the Oceans in the Biogeochemistry of Iron in Seawater, edited by D. Turner and K. Hunter, John Wiley, New York, in press, 1999.

Johnson, K.S., K.H. Coale, V.A. Elrod, and N.W. Tindale, Iron photochemistry in seawater from the equatorial Pacific, Mar. Chem., 46, 319-334, 1994.

Johnson, K.S., R.M. Gordon, and K.H. Coale, What controls dissolved iron concentrations in the world ocean?, Mar. Chem., 57, 137-161, 1997a.

Johnson, K.S., R.M. Gordon, and K.H. Coale, What controls dissolved iron concentrations in the world ocean? Authors' closing comments, Mar. Chem., 57, 181-186, 1997b.

Keigwin, L.D., G.A. Jones, S.J. Lehman, and E.A. Boyle, Deglacial meltwater discharge, North Atlantic deep circulation and abrupt climate change, J. Geophys. Res., 96, 16,811-16,826, 1991.

Keigwin, L.D., W.B. Curry, S.J. Lehman, and S. Johnsen, The role of the deep ocean in North Atlantic climate change between 70 and 130 kyr ago, Nature, 371, 323-329, 1994.

Knox, F., and M. McElroy, Changes in atmospheric CO$_2$, influence of marine biota at high latitudes, J. Geophys. Res., 89, 4629-4637, 1984.

Kumar, N., R.F. Anderson, R.A. Mortlock, P.N. Froelich, P. Kubik, B. Dittrich-Hannen, and M. Suter, Increased biological productivity and export production in the glacial Southern Ocean, Nature, 378, 675-680, 1995.

Luther, G.W., III, and J. Wu, What controls dissolved iron concentrations in the world ocean, Mar. Chem., 57, 173-179, 1997.

Mahowald, N., K.E. Kohfeld, M. Hansson, Y. Balkanski, S.P. Harrison, I.C. Prentice, M. Schulz, and H. Rodhe, Dust sources and deposition during the Last Glacial Maximum and current climate: A comparison of model results with paleodata from ice cores and marine sediments, J. Geophys. Res., in press, 1999.

Martin, J.H., and S.E. Fitzwater, Iron deficiency limits phytoplankton growth in the north-east Pacific subarctic, Nature, 331, 341-343, 1988.

Martin, J.H., S.E. Fitzwater, and R.M. Gordon, Iron deficiency limits phytoplankton growth in antarctic waters, Global Biogeochem. Cycles, 4, 5-12, 1990a.

Martin, J.H., R.M. Gordon, and S.E. Fitzwater, Iron in Antarctic waters, Nature, 345, 156-158, 1990b.

Martin, J.H., et al., Testing the iron hypothesis in ecosystems of the equatorial Pacific Ocean, Nature, 371, 123-129, 1994.

Minas, H.J. and M. Minas, Net community production in "high nutrient-low chlorophyll" waters of the tropical and Antarctic Oceans: Grazing vs iron hypothesis, Oceanol. Acta, 15(2), 145-162, 1992.

Moore, R.M., J.E. Milley, and A. Chatt, The potential for biological mobilization of trace elements from aeolian dust in the ocean and its importance in the case of iron, Oceanol. Acta, 7(2), 221-228, 1984.

Murray, R.W., M. Leinen, and A.R. Isern, Biogenic flux of Al to sediment in the central equatorial Pacific Ocean: Evidence for increased productivity during glacial periods, Paleoceanography, 8, 651-670, 1993.

Murray, R.W., M. Leinen, D.W. Murray, A.C. Mix, and C.W. Knowlton, Terrigenous Fe input and biogenic sedimentation in the glacial and interglacial equatorial Pacific Ocean, Global Biogeochem. Cycles, 9, 667-684, 1995.

Peng, T.-H., and W.S. Broecker, Dynamical limitations on the Antarctic iron fertilization strategy, Nature, 349, 227-229, 1991.

Petit, J.R., L. Mounier, J. Jouzel, Y.S. Korotkevich, V.I. Kotlyakov, and C. Lorius, Paleoclimatological and chronological implications of the Vostok core dust record, Nature, 343, 56-58, 1990.

Powell, R.T., D.W. King, and W.M. Landing, Iron distributions in surface waters of the south Atlantic, Mar. Chem., 50, 13-20, 1995.

Priddle, J., I. Hawes, J.C. Ellis-Evan, and T.J. Smith, Antarctic aquatic ecosystems as habitats for phytoplankton, Biol. Rev., 61, 199-238, 1986.

Rue, E.L., and K.W. Bruland, Complexion of iron(III) by natural organic ligands in the central North Pacific as determined by a new competitive ligand equilibration/adsorptive cathodic stripping voltammetric method, Mar. Chem., 50, 117-138, 1995.

Sarmiento, J.L., and J.C. Orr, Three-dimensional simulations of the impact of Southern Ocean nutrient depletion on atmospheric CO$_2$ and ocean chemistry, Limnol. Oceanogr., 36(8), 1928-1950, 1991.

Sarmiento, J.L., and J.R. Toggweiler, A new model for the role of the oceans in determining atmospheric pCO$_2$, Nature, 308, 621-624, 1984.

Siegenthaler, U., and T. Wenk, Rapid atmospheric CO$_2$ variations and ocean circulation, Nature, 308, 624-626, 1984.

Sunda, W.G. Comment, What controls dissolved iron concentrations in the world ocean? A comment, Mar. Chem., 57, 169-172, 1997.

Sunda, W.G., and S.A. Huntsman, Iron uptake and growth limitation in oceanic and coastal phytoplankton, Mar. Chem., 50, 189-206, 1995.

Sunda, W.G., D.G. Swift, and S.A. Huntsman, Low iron requirement for growth in oceanic phytoplankton, Nature, 351, 55-57, 1991.

Van den Berg, C.M.G., Evidence for organic complexion of iron in seawater, Mar. Chem., 50, 139-157, 1995.

Walsh, J.J., Herbivory as a factor in patterns of nutrient utilization in the sea, Limnol. Oceanogr., 21, 1-13, 1996.

Wenk, T., and U. Siegenthaler, The high-latitude ocean as a control of atmospheric CO$_2$, in The Carbon Cycle and Atmospheric CO$_2$: Natural Variations Archean to Present, Geophys. Monogr. Ser., vol. 32, edited by E.T. Sundquist and W.S. Broecker, pp. 185-194, Washington, D. C., 1985.

Whitfield, M., and D. Turner, The role of particles in regulating the composition of seawater in Aquatic Surface Chemistry: Chemical Processes at the Particle-Water Interface, edited by W. Stumm, pp. 457-493, JohnWiley, New York, 1987.

Wu, J., and G.W. Luther III, Complexation of Fe(III) by natural organic ligands in the northwest Atlantic Ocean by a competitive ligand equilibration method and kinetic approach, Mar. Chem., 50, 159-177, 1995.

Young, R.W., et al., Atmospheric iron inputs and primary productivity: Phytoplankton responses in the North Pacific, Global Biogeochem. Cycles, 5, 119-134, 1991.

Yu, E.-F., R. François, and M. P. Bacon, Similar rates of modern and last-glacial thermohaline circulation inferred from radiochemical data, Nature, 379, 689-694, 1996.

N. Lefèvre, Plymouth Marine Laboratory, Prospect Place, West Hoe, Plymouth PL1 3DH, England, U.K. (nl@pml.ac.uk)

A.J. Watson, School of Environmental Sciences, University of East Anglia, Norwich NR4 7TJ, England, U.K. (a.watson@uea.ac.uk)