KEYNOTE PERSPECTIVE

The sensitivity of atmospheric CO_2 concentrations to input of iron to the oceans

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ABSTRACT

There have been several recent advances in our understanding of the geochemistry of iron and its effect on the marine biota. In this contribution, we highlight two such advances, namely results of the Ironex experiments in the equatorial Pacific and the recent publication of the first global data set for iron concentrations in the oceans. These have profound consequences for our understanding of the factors that set the pre-anthropogenic concentration of carbon dioxide in the atmosphere, and how these may have changed between glacial and interglacial time. Some of these consequences we are able to quantify and explore, but others open new questions for which we have as yet no answers.

1. Iron and the high-nitrate–low-chlorophyll regions

The origin of the "high-nitrate–low-chlorophyll" (HNLC) condition of restricted parts of the world ocean has been a subject of debate for many years, because these regions challenge the "classical" paradigm: that biological utilisation of inorganic carbon and nutrients proceeds at a high rate in surface water unless and until the phosphate and nitrate are reduced to zero. This paradigm works over the large areas of the subtropical gyres, where Ekman transport produces convergence, the supply of nutrients from below is small, and concentrations in surface water are very low. It is also appropriate in regions such as the North Atlantic, where there is abundant nutrient supply from below, but where productivity is also

extremely high. There remain three regions of the world ocean which are HNLC, that is where macro-nutrients remain at the surface year-round but marine productivity levels are not maximal. These regions are the subarctic Pacific, the equatorial Pacific and the Southern Ocean. Fig. 1, which shows annual average nitrate concentrations at the surface, illustrates the extent of these regions.

The origins of HNLC conditions are of interest to marine biologists for obvious reasons. However, they are also of prime interest to geochemists studying the control of the natural (pre-anthropogenic) concentrations of carbon dioxide in the atmosphere. Over time-scales of order 10^2 to 10^5 years, atmospheric CO_2 is governed primarily by equilibrium with the surface ocean. Furthermore, the sites of deep water formation in the polar and sub-polar oceans are more important in this regard than the rest of the oceans (Sarmiento and Orr, 1991; Sarmiento and Toggweiler, 1984). The
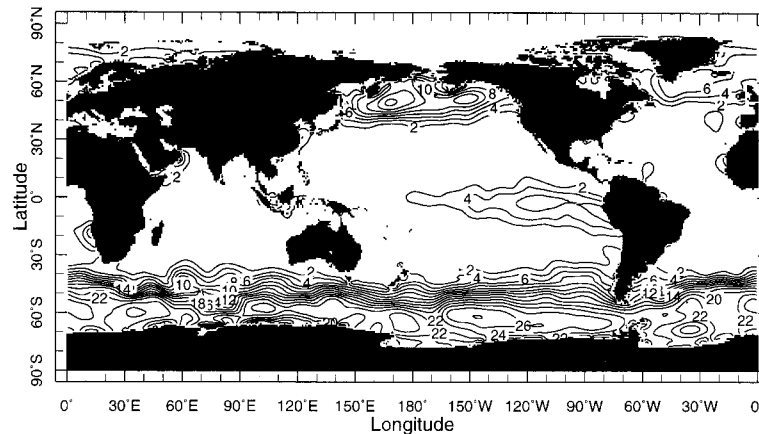
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Fig. 1. Annual average surface ocean nitrate concentrations, from Levitus et al. (1994; figure constructed using the LDEO/IRI online Climate Data Library). The HNLC regions, the subarctic Pacific, equatorial Pacific and Southern Ocean show up as regions of high year-round nutrients. Nutrients are also non-zero on average in the North Atlantic and in regions affected by upwelling such as the Benguela upwelling and the Arabian Sea, but these regions have associated high chlorophyll.

reason for this is that the great majority of mass transfer between the surface and the rest of the ocean occurs at these restricted sites; most of the ocean surface is occupied by relatively warm water which is much less dense than the bulk of the oceans, and therefore mixes with it only slowly. Recent direct measurements confirm that the rate of mixing between these two bodies across the main thermocline of the ocean is very small indeed (Ledwell et al., 1993). But the great majority of the labile carbon on earth is contained in the deep sea. Accordingly, the partitioning of carbon between the atmosphere-plus-surface ocean (which exchange so freely that, on the time scales being considered here, they act as a single reservoir) and the deep ocean, is governed by conditions at the surface of the polar oceans. Since the most extensive of these, the Southern Ocean, is also the largest and most extreme of the HNLC regions, the factors maintaining the HNLC condition in the Southern Ocean are also critical to an understanding of natural CO_2 concentrations. For example, Sarmiento and Orr (1991) found that instantaneous removal of the HNLC condition in the Southern Ocean reduced atmospheric CO_2 by 70 ppm in the space of 100 years.

One of the theories proposed to explain the HNLC condition is that lack of iron supply to these regions restricts the growth of phytoplankton and limits the ecosystem "new production" (that proportion of the primary production which uses upwelling nitrate as its source of nitrogen). This idea, proposed as long ago as the 1930s (Gran, 1931), but more recently associated with the late John Martin, has received support from the results of incubation experiments in all three HNLC regions (Boyd et al., 1996; Martin et al., 1990a; Martin and Fitzwater, 1988; Martin et al., 1989; Martin et al., 1990b; Martin et al., 1991; Price et al., 1991; Takeda and Obata, 1995; Van Leeuwe et al., 1997). In such experiments, samples of seawater, including their in-situ plankton community, are incubated on the deck of a ship. The results of incubators spiked with nanomolar additions of inorganic iron are compared with control incubations. Most of those reported have shown a substantial effect of iron addition. Typically, the the enriched samples show strong growth of diatoms, relatively large cells compared to the dominant initial phytoplankton population. Simulation of net production is not immediate but becomes apparent after 2–3 days, and the controls also show significantly increased net production compared to the initial condition.

The interpretation of such experiments as unequivocal support for the "iron hypothesis" has been questioned (Banse, 1991; Cullen, 1991; Dugdale and Wilkerson, 1990). Among the objec-

tions raised are (a) that study of the in-situ ecosystems show that the majority of the phyto-plankton are growing at near-maximal values, and do not appear to be unduly iron-starved, (b) that grazing by micro-zooplankton is the dominant loss process and might therefore be assumed to be the main limiting factor, and (c) that, in the Antarctic in particular, lack of light may also play a role in limiting the ecosystem productivity, even in summer.

2. The Ironex experiments

In the light of such ongoing uncertainties, in the early 1990s, J. H. Martin and colleagues proposed open-ocean experiments in which patches of surface ocean in the equatorial Pacific would be enriched with nanomolar quantities of iron. The reduction to practice of tracer techniques for the real-time tracking of surface water patches over a period of weeks made it possible to plan these experiments on a practical scale (Watson et al., 1991). The results of Ironex I and Ironex II (which took place in November 1993 and April 1995, respectively) showed unequivocally that iron is an important limiting nutrient in the equatorial Pacific at least (Coale et al., 1996; Martin et al., 1994). In both experiments, addition of iron was accompanied by almost immediate changes in the photosynthetic activity of the phytoplankton (Behrenfeld et al., 1996; Kolber et al., 1994).

In Ironex I, a single addition of iron was made at the start of the experiment which raised ambient concentrations to $\sim 4\, nmol\, kg^{-1}$. Primary pro-duction doubled, and remained high in the fert-ilised patch for about a week following fertilisation (Martin et al., 1994). Initially, there was some net uptake of carbon and nutrients; however, this ceased after about 3 days. After this time, there was little change in the chemistry of the surface water, and the overall biogeochemical signal of the fertilisation was slight (Watson et al., 1994).

During Ironex II, addition of the same total amount of iron was spread over a longer time period, with 3 separate injections totalling about $4\, nmol\, kg^{-1}$ released into the water over a period of several days (Coale et al., 1996). The injection resulted in a massive diatom bloom which peaked 7 days after the start of the experiment, and was accompanied by substantial decreases in surface

water $f CO_2$ (Cooper et al., 1996). Fig. 2, from Cooper et al., shows the drawdown of surface $f CO_2$ on days 6–8 compared to the distribution of tracer marking the spread of the initial iron injection. Diatom growth continued until silica in surface waters was nearly exhausted (K. Johnson and K. Coale, personal communication), sug-gesting that lack of silica was the factor which brought the bloom to a halt. The results of Ironex II are in line with what was predicted from the previously described experiments in incub-ators. Though not conclusively proven, it seems
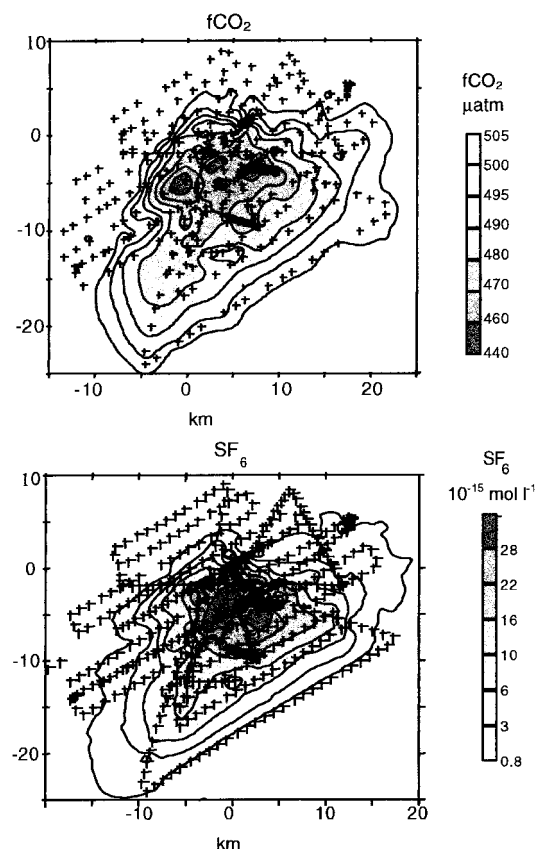
Fig. 2. The spatial distribution of surface in-situ $f CO_2$ on days 6–8 of Ironex II (top panel) compared to the SF_6 tracer distribution which marks where the iron was originally added. Crosses show individual measurements. The detailed correspondence between the two distribu-tions leaves little room for doubt that the two are caus-ally related. Maximum CO_2 drawdowns at the centre of the patch were $\sim 80\,\mu atm$ below the ambient waters in the region. Redrawn from Cooper et al. (1996).

very likely that it was the difference in the time period over which the iron was released that caused the outcomes of Ironex I and II to diverge after 3 days, leading to a much larger effect on surface water carbon dioxide properties in the second experiment than the first.

The simplest interpretation of the Ironex results therefore, is that, in the equatorial Pacific, nano-molar iron concentrations sustained for more than a few days can produce a dramatic shift in the HNLC condition due to promotion of new pro-duction by diatoms, to the point where diatom growth may use up all the available silica. The results also show that iron addition does not by itself inevitably lead to this result, and in particu-lar, that short-lived iron additions affect the eco-system, but not in a way which produces a bloom of diatoms. Though we cannot uncritically extra-polate these results to all the HNLC regions of the world, we can at least hypothesise that similar effects might be observed if such experiments were to be performed in the antarctic or subarctic Pacific.

3. Concentrations of iron in the global ocean

Recently the first data set for concentrations of iron in the ocean with something like global coverage has been published (Johnson et al., 1997). Though there is still very little data by comparison with the more traditional nutrients, the compila-tion of Johnson et al. (1997) is sufficient to show us that iron has a very different geochemistry to other nutrients. In open ocean sites away from the continental margins, the measured deep water concentration of "dissolved" iron is rather con-stant at about 0.6 nM. Iron shows a "nutrient-like" profile in the sense that it is depleted in surface waters compared to the deep ocean. However, it does not display the enrichment of bottom waters in the Pacific over the Atlantic which is characteristic of other nutrient elements. This enrichment is the usual result of the inter-action of vertical fractionation due to the "bio-logical pump" acting on nutrient, with the horizontal flow of deep water from the Atlantic to the Pacific (Broecker and Peng, 1982). The opposite pattern, of enrichment of the deep Atlantic over the Pacific, might be expected if the chief source of iron was dust from the atmosphere,

and the main removal process simple scavenging to particle surfaces. However, the data do not show this pattern very strongly either. It is believed that the main source of iron to the oceans is atmospheric deposition (Duce and Tindale, 1991). The data of Duce et al. (1991) on the pattern of dust deposition shows a very uneven distribution, with regions such as the Southern Ocean receiving 3 or 4 orders of magnitude less dust per unit area than parts of the north Atlantic and north Pacific. For elements such as lead sourced from the atmo-sphere and removed by simple scavenging to particles which then sink out, this pattern is broadly reflected in the concentrations observed both at the surface and at depth in the sea. But iron in the deep sea does not apparently behave in this way.

The establishment of approximate concentra-tions for iron in the oceans enables a re-assessment of the sources of iron to the HNLC regions. In Table 1, we make order of magnitude comparisons of the flux of iron entering these zones from the atmosphere and from upwelling water. Fluxes of upwelling water are relatively well-constrained from oceanic models. The dust fluxes are much less well known and we allow a factor of 10 uncertainty. The fraction of atmospheric iron which dissolves in sea water is also poorly con-strained and variable, adding further uncertainty to the figures. Nevertheless, it is clear that in the Southern Ocean in particular, the atmospheric flux is negligible compared to the flux due to upwelling. This is probably also the case in the equatorial Pacific, whereas in the subarctic Pacific, either the atmosphere or the ocean source could dominate.

Therefore, the biota of the Southern Ocean today receive essentially all their iron from upwel-ling of deep waters, the same source from which they receive nitrate and phosphate. Today, the molar ratio of Fe:P:N in this water is approxi-mately 1:4400:58000 and we need to compare this to the requirements of the phytoplankton to determine which is limiting. In contrast to the N:P ratio, the Fe:P or Fe:N ratio of plankton is quite variable and species-dependent, with organ-isms adapted to the low-iron environment of the open ocean having a lower iron requirement than those which flourish in coastal ecosystems. However, pelagic diatoms, which seem to be responsible for most of the new production of the

Table 1. *Estimates of aeolian and upwelling iron fluxes for HNLC regions*

	Area (10^{12} m^2)	Upwelling flux (Sv)	Upwelling Fe flux[g] (10^6 mol a^{-1})	Aeolian dust flux[h] (mg m^{-2} a^{-1})	Atmospheric input of soluble Fe[j] (10^6 mol a^{-1})
Equatorial Pacific	18[a]	44[d]	280	10–100	2–100
Antarctic	10.8[b]	25[e]	480	1–10	0.14–6.8
Sub-arctic Pacific	6.2[c]	4.5[f]	86	100–1000	7.8–390

[a] Longhurst et al. (1995) sum of PEQD and PNEC biogeochemical provinces.
[b] Longhurst et al. (1995) sum of ANTA and APLR biogeochemical provinces.
[c] Longhurst et al. (1995) sum of PSAE and PSAW biogeochemical provinces.
[d] Wyrtki (1981).
[e] Stevens and Ivchenko (1997).
[f] Semtner and Chervin (1992).
[g] Calculated as upwelling water flux × (concentration in deep water) where this concentration is 0.6 nM for antarctic and subarctic Pacific, and 0.2 nM for the equatorial Pacific.
[h] Estimates taken from the maps of Duce et al. (1991).
[j] Calculated as 3.5% by weight of the dust flux, with 2% or 10% of this dissolving (L. Spokes, personal communication).

open oceans (Dugdale and Wilkerson, 1998) typically have minimum Fe:C requirements in the range $1:10^5$–2×10^5 (Sunda and Huntsman, 1995) which equates to an Fe:P requirement of $1:1000$ to $1:2000$, assuming C:P ~ 100. Hence, iron is apparently limiting to these organisms in the Southern Ocean by virtue of its "sub-Redfieldian" abundance in deep ocean water. The amount of phosphate which the biota should take up before running out of iron might be predicted to be 1000–2000 times the deep water iron concentration, or 0.6–1.2 μM. This is indeed roughly the difference between deep water phosphate and surface ocean phosphate in the Southern Ocean, so what we know about concentrations there is consistent with the notion that the deep-water Fe concentration plays a fundamental rôle in limiting productivity and therefore carbon dioxide uptake in this region.

4. Consequences for atmospheric CO$_2$

The reasoning outlined above leads us to the conclusion that the processes which set upwelling-water iron concentrations in the southern ocean must have a substantial effect on the natural concentration of CO$_2$ in the atmosphere. What then are those processes? Johnson et al. (1997) suggest that the concentration of iron in the deep sea is controlled by the abundance of organic ligands which bind the iron and prevent it from

being scavenged to particle surfaces, which otherwise occurs on time scales of order 100 years. There is good evidence that >99% of all iron in sea water exists in such organically bound form (Rue and Bruland, 1995; Rue and Bruland, 1997; Van den Berg, 1995), and this is likely to mean that the chemical behaviour of iron in seawater is very different from that of other nutrients. The interpretation of Johnson et al. (1997) has been questioned (Boyle, 1997) on the grounds that a suitable combination of "conventional" geochemical process such as nutrient cycling and scavenging on particles might be responsible for the observed near-constancy of deep water concentrations. However, a recent model of the geochemical cycle of iron in seawater which we constructed (Lefèvre and Watson, submitted) led us to the same conclusion as that of Johnson et al. (1997). To explain reasonably constant deep water concentrations, we found it necessary to include ligands that bound strongly to iron and prevented it from being scavenged onto particle surfaces, and which themselves had a near-constant concentration in the deep sea.

Unfortunately, the origin, structure, lifetime and fate of these compounds remain obscure. If they are present in the deep ocean in near-constant concentrations, they must either have a long lifetime, well in excess of the time-scale for ocean circulation of ~ 1000 years, or else they must be continually being produced and consumed in situ by the biota there, presumably by bacteria. Even

this second possibility seems unsatisfactory as a mechanism to produce nearly constant concentrations everywhere in the deep sea; one might naturally expect higher concentrations near the surface where there is more biological activity, and in recently formed deep water. If the lifetime of the ligands is measured in tens of thousands of years, it is even possible that they are not sourced from the marine biota at all, but derive from terrestrial vegetation and enter the sea via rivers. Our ignorance stems from the fact that their concentrations are very small, representing only one part in 10^4 or less of the dissolved organic matter in seawater, which is itself very dilute.

Besides being dependent on ligand concentrations, it is also probable that deep-water concentration of iron will respond to some extent to changes in the input of iron to the oceans as atmospheric dust. The degree to which the concentration responds to changes in the input depends on the lifetime against scavenging of Fe that is not bound to a ligand. If this is ~ 100 years as Johnson et al. (1997) suggest, our study suggests one ought to expect modestly higher concentrations in Atlantic deep water than Pacific deep water, due to the proximity of the Saharan dust source. There are as yet insufficient concentration data to be conclusive about this possibility. Such a lifetime would also mean that the supply of iron to the Southern Ocean would be sensitive to changes in the global source. This occurs because the upwelling water comes from Circumpolar Deep Water which itself consists in part of North Atlantic Deep Water, entering the Southern Ocean from the north Atlantic on a time-scale of order ~ 100 years. A larger source of iron into the Atlantic, such as might have occurred during the colder and drier glacial climate, might therefore result in lower atmospheric CO_2 by the mechanism of stimulation of Southern Ocean productivity. Fig. 3 shows the sensitivity of atmospheric CO_2 to the global atmospheric iron source according to one model (Lefèvre and Watson, submitted). The lower atmospheric CO_2 may contribute further to the cooling and drying of the climate, leading to a positive feedback.

The colder, drier and windier glacial climate, if it resulted in a substantially higher burden of atmospheric dust, might plausibly have led to a global increase in the productivity of pelagic diatoms. In many locations, this would have been
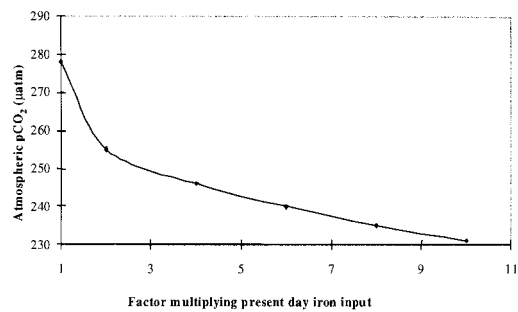

Fig. 3. Change in atmospheric CO_2 in response to an increase of the atmospheric flux of iron to the oceans everywhere, for one realisation of a model of the biogeochemical cycle of iron and its coupling with the carbon cycle (Lefèvre and Watson, submitted). Atmospheric pCO_2 is plotted as a function of the factor multiplying the atmospheric flux of iron.

at the expense of other classes of organisms, such as calcite depositing phytoplankton. These generally produce less organic carbon sinking flux than diatoms, but contribute to the rain of calcium carbonate to the sediments. There are many locations in which surface water silica concentrations are near to zero, and it might be argued that here, diatom productivity could not increase because of silica limitation. However, Hutchins and Bruland (1998) have recently observed that diatoms growing in more iron-rich environments used substantially less silica than in iron-poor conditions. This suggests that increasing iron supply could enhance diatom productivity even in regions that are low in silica.

Thus, the marine biota under a glacial climate might be expected to be more diatom-dominated than the present day. One consequence of this might be an increase in the "rain ratio" of organic to inorganic carbon reaching sediments. Archer and Maier-Reimer (1994) have previously raised the possibility that such a shift might also have contributed to glacial-to-interglacial change in atmospheric CO_2. Organic carbon remineralised in the near-surface sediments causes the pore water to become richer in carbon dioxide, lowering the pH and making the sediment more corrosive to calcium carbonate. Some calcite therefore dissolves and percolates back into the overlying sea water, where it increases the alkalinity, in time, of the whole ocean. This results in lower CO_2 concentrations in the atmosphere in equilibrium with

this ocean. This mechanism has the advantage that it predicts higher pH in the glacial ocean, which is in agreement with proxy evidence from boron isotopes (Sanyal et al., 1995). It would add to the net reduction of atmospheric CO$_2$ in glacial time, being additional to any reduction due to the direct draw-down effect of iron stimulation increasing the productivity of the HNLC areas.

5. Conclusion

It has long been recognised that changes in the ecology of the oceans could have effects on climate by changing the chemical composition of surface sea water, which in turn affects atmospheric CO$_2$ (Broecker and Peng, 1982). However, it has been difficult to identify mechanisms that might bring about such ecological changes in the marine biota. The recognition that diatoms in particular respond to changes in iron concentrations provides one such mechanism by which global change might induce a shift in the ecological balance of the oceans, which in turn may feed back to further change the climate. However, the recognition that iron supply is important in setting the natural concentration of atmospheric CO$_2$ poses a whole set of new questions for which we have as yet no answers. The chemistry of iron in the oceans is far more complex than that of other nutrients, and our knowledge of what controls iron concentrations is at present rudimentary.

6. Acknowledgement

REFERENCES

Archer, D. and Maier-Reimer, E. 1994. Effect of deep-sea sedimentary calcite preservation on atmospheric CO$_2$ concentration. *Nature* **367**, 260–263.

Banse, K. 1991. Rates of phytoplankton cell-division in the field and in iron enrichment experiments. *Limnology and Oceanography* **36**, 1886–1898.

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

Boyd, P. W., Muggli, D. L., Varela, D. E., Goldblatt, R. H., Chretien, R., Orians, K. J. and Harrison, P. J. 1996. In-vitro iron enrichment experiments in the NE subarctic Pacific. *Marine Ecology-Progress Series* **136**, 179–193.

Boyle, E. 1997. What controls dissolved iron concentrations in the World Ocean? A comment. *Marine Chemistry* **57**, 163–167.

Broecker, W. S. and Peng, T.-H. 1982. Tracers in the sea. Eldigio Press, Palisades, New York.

Coale, K. H. et al. 1996. A massive phytoplankton bloom induced by an ecosystem-scale iron fertilization experiment in the equatorial Pacific Ocean. *Nature* **383**, 495–501.

Cooper, D. J., Watson, A. J. and Nightingale, P. D. 1996. Large decrease in ocean-surface CO$_2$ fugacity in response to in-situ iron fertilization. *Nature* **383**, 511–513.

Cullen, J. J. 1991. Hypotheses to explain high-nutrient conditions in the open sea. *Limnology and Oceanography* **36**, 1578–1599.

Duce, R. A. and Tindale, N. W. 1991. Atmospheric transport of iron and its deposition in the ocean. *Limnology and Oceanography* **36**, 1715–1726.

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

Dugdale, R. C. and Wilkerson, F. P. 1990. Iron addition experiments in the Antarctic: a re-analysis. *Global Biogeochemical Cycles* **4**, 13–19.

Dugdale, R. C. and Wilkerson, F. P. 1998. Silicate regulation of new production in the equatorial Pacific upwelling. *Nature* **391**, 270–273.

Gran, H. H. 1931. On the conditions for the production of plankton in the sea. *Rapp. Proc. Verb. Cons. Int. Explor. Mer.* **75**, 37–46.

Hutchins, D. A. and Bruland, K. W. 1998. Iron-limited diatom growth and Si:N uptake ratios in a coastal upwelling regime. *Nature* **393**, 561–564.

Johnson, K. S., Gordon, R. M. and Coale, K. H. 1997. What controls dissolved iron concentrations in the world ocean? *Marine Chemistry* **57**, 137–161.

Kolber, Z. S., Barber, R. T., Coale, K. H., Fitzwater, S. E., Greene, R. M., Johnson, K. S., Lindley, S. and Falkowski, P. G. 1994. Iron limitation of phytoplankton photosynthesis in the equatorial pacific-ocean. *Nature* **371**, 145–149.

Ledwell, J. R., Watson, A. J. and Law, C. S. 1993. Evidence for slow mixing across the pycnocline from an open-ocean tracer-release experiment. *Nature* **364**, 701–703.

Lefèvre, N. and Watson, A. J. 1999. Modelling the geo-

chemical cycle of iron in the oceans and its impact on atmospheric CO_2 concentrations. *Global Biogeochemical Cycles*, submitted.

Levitus, S., Burgett, R. and Boyer, T. 1994. *World Ocean Atlas 1994*, vol. **3**, *Nutrients*. NOAA Atlas NESDIS, US Dept of Commerce, Washington DC.

Longhurst, A., Sathyendranath, S., Platt, T. and Caverhill, C. 1995. An estimate of global primary production in the ocean from satellite radiometer data. *Journal of Plankton Research* **17**, 1245–1271.

Martin, J. H., Broenkow, W. W., Fitzwater, S. E. and Gordon, R. M. 1990a. Does iron really limit phytoplankton production in the offshore sub-arctic Pacific — yes, it does — a reply. *Limnology and Oceanography* **35**, 775–777.

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

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

Martin, J. H., Gordon, R. M., Fitzwater, S. and Broenkow, W. W. 1989. Vertex–phytoplankton iron studies in the Gulf of Alaska. *Deep-Sea Research*, Part A, *Oceanographic Research Papers* **36**, 649.

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

Martin, J. H., Gordon, R. M. and Fitzwater, S. E. 1991. The case for iron. *Limnology and Oceanography* **36**, 1793–1802.

Price, N. M., Andersen, L. F. and Morel, F. M. M. 1991. Iron and nitrogen nutrition of equatorial Pacific plankton. *Deep-Sea Research*, Part A, *Oceanographic Research Papers* **38**, 1361–1378.

Rue, E. L. and Bruland, K. W. 1995. Compelxation 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. *Marine Chemistry* **50**, 117–138.

Rue, E. L. and Bruland, K. W. 1997. The rôle of organic complexation on ambient iron chemistry in the equatorial Pacific Ocean and the response of a mesoscale iron addition experiment. *Limnology and Oceanography* **42**, 901–910.

Sanyal, A., Hemming, N. G., Hanson, G. N. and Broecker, W. S. 1995. Evidence for a higher pH in the glacial ocean from boron isotopes in foraminifera. *Nature* **373**, 234–236.

Sarmiento, J. L. and Orr, J. C. 1991. 3-dimensional simulations of the impact of southern ocean nutrient depletion on atmospheric CO_2 and ocean chemistry. *Limnology and Oceanography* **36**, 1928–1950.

Sarmiento, J. L. and Toggweiler, J. R. 1984. A new model for the role of the oceans in determining atmospheric PCO_2. *Nature* **308**, 621–624.

Semtner, A. J. and Chervin, R. M. 1992. Ocean general-circulation from a global eddy-resolving model. *Journal of Geophysical Research-Oceans* **97**, 5493–5550.

Stevens, D. P. and Ivchenko, V. O. 1997. The zonal momentum balance in an eddy-resolving general-circulation model of the southern ocean. *Quarterly Journal of the Royal Meteorological Society* **123** (540 Pt. B), 929–951.

Sunda, W. G. and Huntsman, S. A. 1995. Iron uptake and growth limitation in oceanic and coastal phytoplankton. *Marine Chemistry* **50**, 189–206.

Takeda, S. and Obata, H. 1995. Response of equatorial Pacific phytoplankton to subnanomolar Fe enrichment. *Marine Chemistry* **50**, 219–227.

Van Leeuwe, M. A., Scharek, R., DeBaar, H. J. W., DeJong, J. T. M. and Goeyens, L. 1997. Iron enrichment experiments in the southern ocean: physiological responses of plankton communities. *Deep-Sea Research*, Part II, *Topical Studies in Oceanography* **44**, 189–207.

Van den Berg, C.M.G. 1995. Evidence for organic complexation of iron in seawater. *Marine Chemistry* **50**, 139–157.

Watson, A. J., Law, C. S., Van Scoy, K. A., Millero, F. J., Yao, W., Friederich, G. E., Liddicoat, M. I., Wanninkhof, R. H., Barber, R. T. and Coale, K. 1994. Minimal effect of iron fertilization on sea-surface carbon-dioxide concentrations. *Nature* **371**, 143–145.

Watson, A. J., Liss, P. S. and Duce, R. A. 1991. Design of a small scale iron enrichment experiment. *Limnology and Oceanography* **36**, 1960–1965.

Wyrtki, K. 1981. An estimate of equatorial upwelling in the Pacific. *Journal of Physical Oceanography* **11**, 1205–1214.