REVIEW

The next generation of iron fertilization experiments in the Southern Ocean

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Of the various macro-engineering schemes proposed to mitigate global warming, ocean iron fertilization (OIF) is one that could be started at short notice on relevant scales. It is based on the reasoning that adding trace amounts of iron to iron-limited phytoplankton of the Southern Ocean will lead to blooms, mass sinking of organic matter and ultimately sequestration of significant amounts of atmospheric carbon dioxide (CO_2) in the deep sea and sediments. This iron hypothesis, proposed by John Martin in 1990 (Martin 1990 *Paleoceanography* **5**, 1–13), has been tested by five mesoscale experiments that provided strong support for its first condition: stimulation of a diatom bloom accompanied by significant CO_2 drawdown. Nevertheless, a number of arguments pertaining to the fate of bloom biomass, the ratio of iron added to carbon sequestered and various side effects of fertilization, continue to cast doubt on its efficacy. The idea is also unpopular with the public because it is perceived as meddling with nature. However, this apparent consensus against OIF is premature because none of the published experiments were specifically designed to test its second condition pertaining to the fate of iron-induced organic carbon. Furthermore, the arguments on side effects are based on worst-case scenarios. These doubts, formulated as hypotheses, need to be tested in the next generation of OIF experiments. We argue that such experiments, if carried out at appropriate scales and localities, will not only show whether the technique will work, but will also reveal a wealth of insights on the structure and functioning of pelagic ecosystems in general and the krill-based Southern Ocean ecosystem, in particular. The outcomes of current models on the efficacy and side effects of OIF differ widely, so data from adequately designed experiments are urgently needed for realistic parametrization. OIF is likely to boost zooplankton stocks, including krill, which could have a positive effect on recovery of the great whale populations. Negative effects of possible commercialization of OIF can be controlled by the establishment of an international body headed by scientists to supervise and monitor its implementation.

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1. Introduction

Iron fertilization of the open ocean, by both natural and artificial means, has been in the limelight ever since John Martin formulated the 'iron hypothesis' (Martin 1990). It postulates that adding iron to nutrient-rich but low productive ocean regions, by dust in the past and artificial fertilization in the future, would stimulate phytoplankton blooms, which would drawdown significant amounts of atmospheric carbon dioxide (CO_2) and, by mass sinking, sequester the carbon for long time scales in the deep ocean and sediments. The hypothesis was welcomed by biogeochemists and palaeoceanographers as a plausible mechanism to explain the lower glacial atmospheric CO_2 levels that coincided with higher dust deposition rates compared with the interglacials. Plankton ecologists on the other hand were sceptical that the trace nutrient iron could limit phytoplankton growth to the same extent as light and the macronutrients, nitrate and phosphorus. Unfortunately, the spectre of wanton commercialization of OIF put the scientific community as a whole on its guard. The precautionary principle was applied and discussions of the iron hypothesis have centred on the possible negative effects (Chisholm *et al.* 2001; Lawrence 2002). However, given the paucity of evidence regarding both its efficacy and the effects it might engender, scepticism of OIF is premature, particularly when compared with other options and in view of the recent consensus on the wide-reaching effects of inevitable climate change (Lampitt *et al.* in press).

Ten OIF experiments have been carried out so far in different oceans by scientists from many countries. Phytoplankton blooms dominated by diatoms have been induced in all but one experiment (SEEDS II), thus solving a long-standing paradox: what regulates the productivity of high-nutrient, low-chlorophyll oceans (Chisholm & Morel 1991)? Despite the overwhelming evidence, acceptance of iron as a growth-limiting factor on a par with light or macronutrient (nitrogen and phosphorus) limitation has been slow (de Baar *et al.* 2005) and basic questions pertaining to the fate of iron-induced bloom biomass are still under debate (Boyd *et al.* 2007). Furthermore, the bio-oceanography community has been slow to explore the new research avenues opened up by OIF experiments, and funding agencies have not been doing their utmost to encourage them.

This lack of enthusiasm is reflected in the proportion of ship time allocated to the OIF experiments (a total of only 11 months over 10 years) in relation to the total research ship time (much greater than 2500 months) available in the same period to the various disciplines of observational oceanography. It has recently been pointed out that the experiments were not designed to address the question of whether iron fertilization is a feasible mitigation measure for ongoing global change (Buesseler *et al.* 2008), implying that they could not have provided the answers attributed to them: that OIF is not likely to be efficient (Buesseler & Boyd 2003), will require massive continuous injections of iron sulphate with a large carbon footprint (Zeebe & Archer 2005) and have negative side effects on the oceans and atmosphere (Lawrence 2002). Clearly, there is a need to develop alternative scenarios based on our current understanding of plankton ecology and ocean biogeochemistry but under consideration of the limiting role played by iron over most of the nutrient-rich open ocean.

The Southern Ocean (SO) is the only ocean region where substantial amounts of the phytoplankton nutrients, nitrate and phosphate in surface waters, supplied by upwelling of deep ocean water in the South, are returned to the deep ocean by downwelling along its northern fringe. In contrast to N and P, the CO_2 remineralized from the breakdown of organic particles can escape to the atmosphere, the amount depending on water temperature and the concentration of atmospheric CO_2. Thus, at pre-industrial CO_2 levels of 280 ppm$v$, the SO was a source, but, with the subsequent rise in CO_2 levels, is now considered a weak sink of atmospheric CO_2 (Le Quéré *et al.* 2007) without productivity changing significantly. It follows that enhancing productivity by OIF will enhance this sink to the extent that CO_2, converted to organic matter by fertilized phytoplankton and exported in sinking particles to the deep ocean, is removed from the surface layer. This can be assessed only in experiments designed for the purpose.

Quantitative assessment of the effects of OIF requires application of models of SO ecology and biogeochemistry embedded in hydrography. However, the predictions of various models developed for the purpose, reviewed by Lampitt *et al.* (in press), differ widely, depending on the parameters employed: in particular, C : Fe ratios of phytoplankton and depth-dependent remineralization rates in the water column relative to the sinking rate of vertical flux. Recent studies of naturally fertilized ecosystems in the vicinity of the SO islands of Crozet (Pollard *et al.* 2007) and Kerguelen (Blain *et al.* 2007) indicate higher C : Fe ratios and higher deep export rates of carbon than those derived from the experiments. Clearly, data from appropriately designed OIF experiments are a prerequisite for running realistic models exploring local and global effects of iron fertilization.

In this paper, we argue that it is high time to launch the next generation of OIF experiments in the SO. We examine the state of Martin's iron hypothesis and show how the current impasse regarding the role of iron on the ecology and biogeochemistry of the SO can be overcome by carrying out a series of experiments specifically designed to assess the magnitude, depth and composition of vertical flux in relation to surface productivity and structure of the pelagic food web. We present a series of hypotheses amenable to testing in future experiments and show how the scientific community can take charge of the situation and prevent the negative effects of OIF commercialization.

2. The concept of iron limitation

Iron has long been suspected to be a growth-limiting factor in the ocean based on well-established facts: its conversion to highly insoluble ferric hydroxide (rust) in alkaline, oxygenated seawater and its obligate requirement by all organisms. Furthermore, the consistently higher plankton productivity of near land compared with open ocean waters of the SO was taken as evidence for the provisioning of trace elements (including iron) from the land and their limiting role away from it (Hart 1942).

The perennially high macronutrient concentrations in large tracts of ocean, the Sub-Arctic and Equatorial Pacific and the entire SO, known as the high-nutrient, low-chlorophyll (HNLC) regions, were considered a paradox compared with the equatorial and high-latitude regions of the Atlantic Ocean where

nutrients were exhausted over much of the growth season. Three mutually inclusive reasons were proposed to explain the HNLC condition: low light levels in the deep mixed layers of high latitudes; iron limitation of phytoplankton growth; and heavier grazing pressure due to life histories of dominant grazers in HNLC regions. Although light limitation cannot apply to the Equatorial Pacific and zooplankton populations vary widely both seasonally and regionally, iron limitation, the only factor common to all regions, was regarded with scepticism, partly because early iron addition experiments could show no difference between control and iron-supplemented bottles. With hindsight, this was due to contamination of controls by trace amounts of iron.

John Martin's group overcame the contamination problem by applying ultraclean methods to field measurements and bottle experiments. They demonstrated very low iron concentrations in HNLC waters and, in bottle experiments, a strong response of natural plankton to iron addition, in striking contrast to the absence of growth in control bottles (Martin & Fitzwater 1988). This evidence failed to convince many in the bio-oceanography community but biogeochemists took up the challenge more readily and have since opened a booming marine trace metal field (Jickells *et al.* 2005). Not surprisingly, most of the OIF experiments focused on biogeochemical processes with much less attention paid to the underlying ecological processes unfolding at the species level.

The reluctance of bio-oceanographers to place iron limitation of phytoplankton growth on an equal footing with light or macronutrients can be attributed to several reasons. Thus, the issue of whether N or P is the primary limiting nutrient in oceans relative to lakes (where P is long accepted as the limiting nutrient) was hotly debated for both coastal eutrophic waters as well as the open ocean. However, the concept was not transferred to iron by the mainstream community, possibly because many of the scientists involved were working in coastal areas where iron was not an issue. Indeed an early, albeit inadvertent, iron fertilization experiment was carried out by a titanium factory in the form of acid waste dumping in the North Sea where no noticeable effects on phytoplankton productivity were reported. The practice was stopped due to popular protest and the acid waste is now converted to ferrous sulphate and applied to lawns and sewage treatment plants.

Apparently, the methodological problems associated with contamination-free measurements of iron as well as maintenance of iron-clean conditions for experimentation have deterred many biological laboratories from studying the role of iron. Lack of clarity regarding the sources and availability of iron to offshore phytoplankton—how much of it upwells with deep water; how much is introduced by dust (Cassar *et al.* 2007); and how much is retained in the surface layer by binding to organic molecules with an affinity for iron (ligands; Jickells *et al.* 2005)—is another factor hindering the acceptance of iron limitation by mainstream bio-oceanographers. Thus, the sources of iron enabling the annual spring bloom in the open N. Atlantic, which set this ocean apart from the other high-latitude oceans, are still not unequivocally established.

Furthermore, there are indications that the iron demand of coastal versus oceanic phytoplankton differ (Strzepek & Harrison 2004) implying that the impact of iron deficiency, unlike that of macronutrients, is also a question of adaptation, hence species composition. However, this view overlooks the extensive, obligate role played by iron in the cellular machinery where it is as

much an essential building block as, for example, phosphate. Both chlorophyll synthesis and nitrate reduction, the two gateways to light and macronutrient usage, respectively, require iron. Thus, by increasing cellular chlorophyll, iron-sufficient phytoplankton can shade adapt, thereby improving the efficiency of light usage (Gervais *et al.* 2002). The accompanying disadvantage of suffering photodamage under calm sunny conditions is of minor importance in the cloudy, stormy SO.

An example for the reluctance to accept the limiting role of iron is encapsulated in a sentence from a recent review of iron fertilization experiments (de Baar *et al.* 2005): 'Hence having dumped a total of 8975 kg of Fe into HNLC waters and using approximately 1 year of shiptime, we may conclude that light is the ultimate determinate of the phytoplankton biomass response'. This statement is based on a comparison of changes in the concentrations of dissolved and particulate properties measured in the various experiments that vary with depth of the mixed layer. The lower chlorophyll concentrations induced by OIF in deeper water columns are interpreted as light limitation. However, budgetary analyses are based not on concentration (g C m^{-3}) but on the magnitude of biomass, which is given by the total stock in the mixed layer water column: concentration multiplied by mixed layer depth (g C m^{-2}). It is the magnitude of the stock (the amount of CO_2 fixed in the water column) that determines the amount of CO_2 exchanged between atmosphere and ocean and the amount that can sink to the deep sea. Indeed, the deeper the mixed layer, the larger the amount of biomass that can be built up, given sufficient iron, owing to the larger nutrient inventory of the deeper water column.

The dilution factor, which increases with depth of the mixed layer, has several different effects on the rate of biomass build-up and its eventual fate. Thus, the deeper the depth of mixing the smaller the percentage of the phytoplankton population within the euphotic zone (the layer where sufficient light is available to enable net growth), which will accordingly slow population growth rate (Smetacek & Passow 1990). The efficiency of light usage by phytoplankton will also be lower owing to attenuation by the deeper water column. However, these effects on the rate of biomass accumulation can be partly compensated by shade adaptation, which effectively increases the depth of the euphotic zone (Gervais *et al.* 2002), and by the reduction in grazing pressure due to the greater dilution of algal cells that decrease predator/prey encounter rate (Landry & Hassett 1982). Algal concentration could also affect the rate of aggregation of cells and chains into flocks (marine snow) and hence magnitude of export from the surface and sinking rate through the deep water column. However, the relevant threshold concentrations of these effects need to be quantified in further experiments.

The fact that all SO OIF experiments induced blooms in a range of mixed layer depths and from spring to late summer (Boyd *et al.* 2007) indicates that iron availability and not light or grazing controlled build-up of biomass. Thus, the standing stock of chlorophyll attained by the EisenEx bloom in a 70 m mixed layer after 21 days (200 mg Chl m^{-2}) was the same as that reached by the SEEDS I bloom in the North Pacific following nitrate exhaustion after 13 days in a 10 m deep layer (Tsuda *et al.* 2003). Field observations also demonstrate that, apart from the winter months, light availability cannot be regarded as a limiting factor for phytoplankton biomass build-up. Standing stocks of more than 200 mg

chlorophyll m^{-2}, equivalent to that of North Sea spring blooms but in threefold deeper mixed layers, have been recorded along the Polar Front (Bathmann *et al.* 1997) and continental slope (Turner & Owens 1995). Indeed, the standing stock of the latter diatom bloom of 7 mg Chl m^{-3} homogeneously distributed in a 70 m mixed layer, stretching in a band along the shelf break of the western Antarctic Peninsula, ranks among the highest recorded in the ocean. Such a standing stock (approx. 15 g C m^{-2}) could also be reached by OIF if the patch were large enough to prevent dilution with outside water. Clearly, this is a best-case scenario highlighting the need for more ambitious experiments.

Over the past decades, environmental scale experiments carried out by terrestrial and lake ecologists have revealed unexpected fundamental insights on various relationships between ecological and biogeochemical processes. So, when the first *in situ* OIF experiments IronEx I and II demonstrated that a patch of surface ocean, marked with sulphur hexafluoride (SF$_6$), could be successfully manipulated and followed for a significant period of time (Martin *et al.* 1994; Coale *et al.* 1996), the feat was hailed as the transition of ocean ecology from an observational to an experimental science (Frost 1996). Nevertheless, the response since then has been muted.

If only 10 per cent of the ship time available to the relevant chemical, biological and geological oceanography disciplines had been dedicated to carrying out OIF experiments, we would now be discussing the results of at least 30 experiments, of which one or more would be large-scale, long-term, multiship international projects akin to the North Atlantic Bloom Experiment coordinated by JGOFS in 1988 (Ducklow & Harris 1993). Such an experiment would by now have quantified the fate of iron-fertilized bloom biomass, provided new insights on the reaction of bacteria and zooplankton communities and their predators to enhanced productivity and monitored the reaction of the deep-sea benthos to an enhanced food supply. Furthermore, insights into the much debated relationship between species diversity and ecosystem productivity could also have been effectively addressed by OIF. In short, we would have answers to the open questions raised in recent reviews of OIF (de Baar *et al.* 2005; Boyd *et al.* 2007; Lampitt *et al.* in press) and acquired many more unexpected insights on pelagic ecosystem structure and functioning and their impact on the deep sea and sediments.

Cost, pollution and expertise cannot be the reasons for the lack of enthusiasm for OIF experiments. Because the ship operates in much the same place, *in situ* experiments actually burn less fuel than conventional transect oceanography racing from station to station. Ferrous sulphate required is sold at low cost in garden shops to improve lawns for which the recommended dosage is 20 g m^{-2}. The dosage required to fertilize a bloom is 0.05 g m^{-2} for a 50 m deep mixed layer. Clearly, hazardous impurities in the commercially available ferrous sulphate will be diluted to insignificant levels. Dispersing iron is straightforward and using SF$_6$ as a tracer is no longer required as other easily monitored parameters such as photosynthetic efficiency, increasing chlorophyll and declining pCO$_2$ accurately track the patch. Running the experiment is not very different from interdisciplinary observational oceanography. Clearly, the prerequisites for oceanographic experimentation have long been in place.

3. The efficacy of iron fertilization

A key question addressed by the iron hypothesis pertains to the sources and sinks of atmospheric CO_2 over glacial/interglacial climate cycles that are of obvious relevance to future OIF. Since more or less the same amount of CO_2—approximately 210 Gt (the difference between 180 and 280 ppm$v$)—has appeared and disappeared from the atmosphere over the past four cycles (Petit *et al.* 1999), it seems logical to assume that the same process and its cessation will have been responsible for removing and returning the CO_2. However, we are far from understanding the processes regulating atmospheric CO_2 levels (Falkowski *et al.* 2000), given that its turnover time at the pre-industrial inventory of approximately 600 Gt was approximately 4 years. Primary production and its subsequent remineralization is responsible for the lion's share—65 and 40 Gt yr^{-1} by land plants and marine phytoplankton, respectively (Falkowski *et al.* 1998; Haberl *et al.* 2007)—the remainder exchanged with the oceans by seasonal cooling and warming combined with replacement of surface water by upwelling and downwelling (the physical solubility pump). Given the high turnover rate combined with the broad range of interannual variability observed at regional scales in both marine and terrestrial productivity, e.g. over El Niño cycles, the near constancy of CO_2 levels over time scales of decades to centuries is remarkable: a 10 per cent change on either side of the balance would result in halving or doubling of atmospheric CO_2 concentrations within 50 years.

Net losses and gains to the CO_2 inventory that would have an effect on time scales of more than 10^4 years are burial in ocean sediments—estimated at 0.02 Gt yr^{-1} (Tyson 1995)—and outgassing from volcanic activity, respectively, which must balance each other, given the near-constant concentrations prevailing for periods of stability over thousands of years between the transitional phases indicated by ice core records (Petit *et al.* 1999). These longer term steady states are again remarkable given that they maintain different CO_2 concentrations and have repeated themselves over six cycles during the past 650 000 yrs (Siegenthaler *et al.* 2005). It should be pointed out that the transitions between warm and cold states differ inasmuch as CO_2 removal takes place gradually, with intermediate steady states, over tens of thousands of years, whereas its release is much more rapid: a few thousand years. This pattern, but not its triggering events, coincides with that of dust in the ice core records: a key factor in the iron hypothesis.

The amount of CO_2 missing during the glacials is equivalent to approximately one-third the biomass of the terrestrial biosphere, the magnitude of which is a direct function of annual rainfall exhibited by the gradient from rainforests to deserts. Owing to the drier glacial climate, the area covered by vegetation was substantially smaller than during interglacials, so the carbon released by retreating forests and wetlands during glacials would also have to be 'sunk' by the same process removing CO_2 from the atmosphere. Hence, we are left with the ocean as the most likely source and sink of atmospheric CO_2. It contains 50 times more carbon than present in the atmosphere. Most of this carbon is bound in bicarbonate and carbonate anions but approximately 1 per cent is present as dissolved $CO_2 + H_2CO_3$. The concentration of CO_2 in the surface layer is in equilibrium with the atmosphere but deep ocean water has excess CO_2 due to remineralization of organic matter transported there by the biological

carbon pump (BCP; Lampitt *et al.* in press). If, in a thought experiment, the BCP were shut down but ventilation of the deep ocean by thermohaline circulation is maintained at today's rate of 1000 years, atmospheric CO_2 concentrations would increase approximately twofold (Maier-Reimer *et al.* 1996), implying that the rate of long-term sequestration (centuries) will be on average $1.2 \, \text{Gt yr}^{-1}$ over a full ventilation cycle of 1000 years. Total export production (organic carbon sinking out of the surface mixed layer) in today's ocean is estimated at $16 \, \text{Gt yr}^{-1}$ (Falkowski *et al.* 1998), implying that most of the sinking carbon flux is retained close to the surface from where CO_2 is recycled with the atmosphere on decadal time scales. This is consistent with the models of depth-dependent organic matter remineralization in the deep water column (Martin *et al.* 1987).

A voluminous literature has been developed around the interpretation of data gathered from ice cores and ocean sediments as evidence for and against the iron hypothesis. The bulk of productivity proxies (indirect indicators of surface productivity such as stable isotope ratios of C and N) recorded in the sediments does not support higher glacial productivity of the Antarctic circumpolar current (ACC) (Anderson *et al.* 2002). However, interpretation of the proxies is fraught with uncertainty and new, less ambiguous proxies need to be identified to achieve progress in the field. One such proxy are the resistant spores of the diatom genus *Chaetoceros* characteristic of dense phytoplankton blooms that have been shown to dominate the fossil assemblage over a much larger area of the Atlantic ACC than they do in modern sediments, implying that phytoplankton blooms were much more extensive over glacial periods (Abelmann *et al.* 2006). Indeed, as we shall see below, large-scale OIF experiments provide an ideal framework to test the hypotheses underlying interpretations of the various proxies.

4. Is the current opposition to OIF justified?

Most of the arguments against OIF invoke worst-case scenarios justified by the precautionary principle, but these need to be weighed against best-case scenarios on the basis of cost and benefit within the context of the global biosphere. For example, two often-cited potential impacts of OIF are (i) the organic matter produced may be recycled in the upper part of the water column resulting in CO_2 sequestration on a time scale of decades rather than centuries expected from deeper organic matter export and (ii) excessive oxygen consumption by decomposition of organic matter in a restricted subsurface layer would create conditions conducive for the production of nitrous oxide (N_2O) and methane (CH_4). Since these gases have higher global warming potentials than CO_2, it is argued that their release to the atmosphere might offset the gains of CO_2 uptake by the ocean (e.g. Fuhrman & Capone 1991). However, ocean methane production is largely restricted to the sediments underlying intense upwelling regions of low latitudes (Bakun & Weeks 2004), so oceans as a whole are a minor player in the atmospheric CH_4 budget (Crutzen 1991). Even in the most intense oceanic oxygen minimum zones (OMZs), CH_4 production does not occur, except perhaps within microanaerobic sites in the interior of particles (e.g. Jayakumar *et al.* 2001). By contrast, oceans are estimated to account for one-quarter to one-third of the total (natural + anthropogenic) N_2O inputs to the

atmosphere (Nevison *et al.* 2004). Moreover, N_2O cycling—production as well as consumption—is very sensitive to the ambient oxygen concentration in the low range (less than approx. 0.5 ml l^{-1}); hence, its enhanced production as a result of OIF deserves a thorough investigation.

N_2O measurements have been made during two of the SO OIFs—the Southern Ocean Iron Enrichment Experiment (SOIREE; Law & Ling 2001) and the European Iron Fertilization Experiment (EIFEX; Walter *et al.* 2005). Whereas some accumulation of N_2O was found to occur within the thermocline underlying the SOIREE patch, no such increase was observed during EIFEX over a threefold longer period. The discrepancy was attributed by Walter *et al.* to the rapid sedimentation of organic particles to the deep ocean, which was also reflected in barium vertical distribution during EIFEX (Jacquet *et al.* 2008). Thus, the depth of remineralization of organic matter produced as a result of OIF will determine not only the storage time in the ocean of the carbon sequestered from the atmosphere, but also the climatic feedback by N_2O. Moreover, the magnitude and even the nature of this feedback would be strongly dependent on the location as well as duration of fertilization, as shown by the modelling study conducted by Jin & Gruber (2003). These authors found that while enhanced production of N_2O could almost completely offset the radiative benefit of OIF in the tropics, this offset would be much smaller in the SO (6–18% in the case of large-scale (approx. 100 million square kilometres) and long-term (100 years) fertilization). This difference arises from the differential effect of the organic carbon mineralization on the subsurface oxygen distributions in the two regions. That is, owing to the high oxygen concentrations in subsurface waters of the SO, the volume of water with low oxygen concentration (approx. 0.5 ml l^{-1}, below which the production of N_2O increases nonlinearly) developed as a result of fertilization will be much smaller than in the tropics where the mesopelagic oxygen minimum is already quite intense and expanding (Stramma *et al.* 2008). In fact, the model results suggest a relaxation of the tropical OMZs as a result of a decrease in export production caused by the lower preformed nutrient concentrations in intermediate waters at their source following fertilization of the SO (Sarmiento & Orr 1991; Jin & Gruber 2003).

On the other hand, the deep-water oxygen concentrations may be expected to fall everywhere in the oceans if the particles emanating from the fertilized blooms sink to the deep sea. This can be expected because massive deep sinking of diatom cells and chains in the aftermath of natural blooms is a well-known phenomenon (Smetacek 1985) that results in accumulation of fluffy layers on the deep-sea floor underlying productive waters (Beaulieu 2002). Because the volume of the deep ocean is three to four times greater than the mesopelagic layer, where N_2O production occurs due to hypoxia, diatom bloom sinking results in dilution of the organic matter, hence also the oxygen deficit resulting from its breakdown. The dilution effect on deep water oxygen depletion can, in fact, have a beneficial effect on atmospheric CO_2 content (Boyle 1988; Sarmiento & Orr 1991). Thus, the palaeoceanographic evidence from the Indian Ocean and Pacific Ocean suggests a rearrangement of the vertical chemical structure during glacial periods with the deep waters being more oxygen depleted (Kallel *et al.* 1988; Galbraith *et al.* 2007). The atmospheric N_2O concentration during the last glacial maximum reached a minimum of 200 ppb*v* or less (Spahni *et al.* 2005). Thus, if the decrease in atmospheric CO_2 during glacial periods was due to

sequestration of carbon in the deep ocean by enhanced SO export, as proposed by Martin, this could account for the inferred lower deep-water oxygen concentrations. Apparently, this oxygen depletion did not lead to an increase in atmospheric N_2O. It would not be unreasonable to assume that artificial OIF would not produce an opposite trend. According to Bakun & Weeks (2004), the projected intensification of low-latitude coastal upwelling due to global warming is likely to result in the spreading of extreme hypoxia and greenhouse gas build-up conditions now regularly observed off Namibia. If true, then diverting nutrients from source waters of coastal upwelling to the deep sea and sediments by OIF will have an additional mitigation effect by constraining low-latitude, coastal N_2O and CH_4 production resulting from the feedback effects of global warming.

The production of other climatically important gases such as dimethyl sulphide (DMS) also needs to be investigated in greater detail through additional observations and modelling. The OIF experiments have been found to typically increase concentrations of DMS and its precursor dimethylsulphoniopropionate (DMSP), by a factor of 3 (Turner *et al.* 2004). Increases of this magnitude, if occurring globally, could lead to atmospheric cooling by 1–2°C (Gunson *et al.* 2006; Liss 2007), which must also be considered while evaluating the impacts and benefits of OIF.

The upper limit for CO_2 drawdown by ocean scale application of OIF is set by the average nitrate concentration (approx. 20 mmol m^{-3}) left in the surface mixed layer (approx. 50 m depth) of the entire ice-free SO (approx. 50×10^6 km^2) at the end of the summer assuming the Redfield ratio of C : N of 6 : 1. Removal of all nitrate at one fell sweep would amount to approximately 4 Gt of carbon. The rate of renewal of nitrate by upwelling deep water is 3–4 years implying that approximately 1 Gt of CO_2 is the minimum amount that could be taken up by an iron-replete SO. More sophisticated models suggest that OIF of the SO can reduce atmospheric CO_2 by over 60 ppm$v$ (Jin & Gruber 2003). Clearly, this is no substitute for reducing emissions, yet it is too large to be ignored, again on the basis of the precautionary principle applied in a global warming context.

The carbon footprint of large-scale OIF is not likely to be large. Ferrous sulphate is freely available as an unwanted by-product of the growing titanium industry and used to be dumped in the past. An average factory produces approximately 400 000 tonnes a year and, assuming a range of C : Fe ratios from worst- to best-case scenarios—1000 : 1 to 10 000 : 1—from 14 to 1.4 million tonnes of granular $FeSO_4$ will be required to sequester 1 Gt of carbon. Shipping this amount of iron to the SO would require diversion of a minuscule percentage of the tanker fleet currently transporting 2 billion tonnes of petroleum annually around the globe. The means by which the iron could be added will not be discussed here, but there are a number of options to choose from that harness ACC wind and current fields for dispersal.

5. Designing future OIF experiments

All experiments used the fertilization technique employed in IronEx: releasing a solution of weakly acidified ferrous sulphate into the propeller wash of the ship steaming along tracks at intervals of 1–3 km, for instance, spiralling outward

from a drifting, surface-tethered buoy. One would expect the weakly acidified iron solution to be quickly neutralized by mixing with alkaline seawater and the dissolved iron oxidized to its insoluble state, i.e. colloidal rust particles that would be difficult for phytoplankton to take up. Nevertheless, the results from the experiments demonstrate otherwise. The fact that the added iron was taken up at a ratio of C : Fe of greater than 15 000 : 1 in the SEEDS experiment (Boyd *et al.* 2007), similar to ratios obtained from natural blooms (Blain *et al.* 2007) and laboratory experiments, is proof that the physiological ability to use iron is present in the phytoplankton. In other words, we see no need yet to replace $FeSO_4$.

Small-scale experiments employing several tonnes of $FeSO_4$ have not lost their relevance because they can be carried out at regional scales to test whether the plankton of a given water body at a given season is iron limited or not. For instance, such experiments will help in elucidating the causes of the regime shift that has occurred in the eastern Bering Sea accompanying retreat of the winter ice cover (Smetacek & Nicol 2005). Nutrient and light availability have not changed, yet the annual phytoplankton bloom, which used to occur during melting of the ice cover in early spring, is now delayed by several months resulting in a shift in the timing of the annual peak of food supply to the benthos.

Further testing of the iron hypothesis will require larger scale experiments at sites where the fertilized surface layer is coherent with the underlying deep water column. Such conditions are met within the closed cores of mesoscale eddies that are formed by meanders of frontal jets that enclose a water mass from the adjacent branch of the ACC. Eddies are of two types depending on the direction of rotation: clockwise-rotating eddies enclose a water column—the core of the eddy—from south of the respective front. Owing to its lower temperature compared with the surrounding frontal jet, the core has a smaller volume and appears as a depression in altimeter images of sea surface height. The opposite holds for anti-clockwise eddies that appear as bulges in the images. Such quasi-stationary eddies extend to the sea floor and can have lifetimes of several months. They are approximately 100 km in diameter (including the enclosing frontal jet) and 4 km deep, hence have to be visualized as slowly rotating, flat discs completing a revolution once a week. Such mesoscale eddies are ideal for studying the growth and demise of iron-fertilized blooms all the way down to the underlying sediments but their lifetime is too short for longer term experiments over the growth season.

Experiments carried out in closed cores of eddies have the added advantage that the fertilized patch retains its initial circular shape over the course of the experiment (Cisewski *et al.* 2008) and is not distorted into a streak as happened during SOIREE and the SOFEX north patch (Boyd *et al.* 2000; Bishop *et al.* 2004). Furthermore, the closed core tends to be horizontally homogeneous in its properties; hence, the effects of local patchiness are greatly diminished. The disadvantage is that horizontal mixing within the core results in the patch spreading rapidly, hence diluting the effects of fertilization by mixing with non-fertilized water from within the eddy core (Cisewski *et al.* 2005). The dilution effect can be lessened by taking care to position the patch as close to the centre of the eddy as possible, where current speeds are lowest, hence coherence between the surface and the underlying deep water column greatest. Unfortunately, the connection with the sediment surface is looser because eddies can be displaced

laterally by approximately 30 km in their lifetime (Losch *et al.* 2006). The dilution effect can also be lessened by fertilizing as large an area as feasible from a research ship. The larger the area of a patch the lesser the effects of dilution at its centre. However, the area of the closed core of an average eddy of 100 km diameter is approximately 3000 km², which is approximately 5–50 times the area of the patches fertilized in previous experiments. Clearly, fertilizing the centre of the core is the best option but locating it at sea is not a trivial task.

6. Hypotheses to be tested in future *in situ* experiments

(*a*) *Interpretation of proxies*

Apart from testing the second condition of the iron hypothesis, i.e. determining the magnitude and depth of vertical particle flux from an iron-induced bloom, future *in situ* experiments can address a host of issues currently under investigation with conventional approaches. A central issue in Earth system science, hence also the future of OIF as a mitigation measure, is the influence of evolving biological properties on the global carbon cycle. The role of organisms in shaping and maintaining Earth's atmosphere at geological time scales is universally accepted. Less clear are the potential impacts of changing biology on climate over shorter time scales of decades. Given the short turnover time of atmospheric CO_2 by the biosphere (approx. 4 years), a change in input or output terms of only a few per cent would have a significant impact within decades. So, stability of the global biosphere is a crucial factor in maintaining the steady states that prevailed over the Holocene and the Last Glacial Maximum. It follows that the transitions between steady states could well have been triggered and maintained by positive feedback mechanisms within the terrestrial and marine biospheres that disrupt the checks and balances maintaining glacial or interglacial steady states. The iron hypothesis postulates a balancing mechanism mediating between terrestrial and oceanic biospheres such that, when the land was brown, the oceans were green and took up CO_2, but when the land was green the oceans were blue and released it back to the atmosphere. This alternating desertification of the land and ocean mediated by rainfall and dust and embedded in ocean circulation is too plausible to be discarded on the basis of evidence obtained to date from sedimentary proxies. Clearly, OIF experiments offer a new approach to test the hypotheses underlying interpretation of the various proxies.

(*b*) *Biology of diatom species*

All OIF experiments have reported stimulation of the entire phytoplankton assemblage by iron addition although biomass accumulated almost exclusively in diatoms. Clearly, this algal group is subject to lower mortality rates than the smaller nano-and picophytoplankton of the microbial food web that, because their larger surface: volume ratios render them more competitive in resource uptake, should have higher growth rates than the much larger diatoms (Smetacek 1999). It follows that only diatoms accumulate biomass because they are better defended against pathogens (viruses) and grazers that keep the smaller phytoplankton in check (Smetacek 2002), in all probability by virtue of

their silica shells (Hamm & Smetacek 2007). The diatom species commonly reported from phytoplankton blooms span a size range equivalent to that of the land plants (from herbs to trees). They also differ vastly in shape and thickness of the silica shells, reflected in Si : N ratios from less than 0.5 to more than 3. Some resemble smooth needles, others are embellished with long, barbed spines many times the length of the cells. Clearly, diatom species morphology will have an effect on the rate of aggregation and size of the aggregates in the senescent phase of blooms, hence also on the magnitude and composition of vertical flux.

The blooms in OIF experiments have been dominated by a broad range of diatom species from many centric and pennate families, generally typical of the fertilized region, and including the shapes mentioned above, indicating that they all have the ability to take up iron in the form provided. The fact that different species assemblages dominated the experiments despite the presence of many more species is a strong indication of internal regulation of biomass build-up (Assmy *et al.* 2007). Unfortunately, our understanding of the factors determining species composition of blooms is rudimentary and can be advanced not only by investigating bloom dynamics at the species-specific level under *in situ* turbulence and light fields but also in the presence of the full complement of pathogens and grazers. OIF experiments meet all these conditions and enable one to follow relevant processes in the surface and deeper layers ensuing from a defined perturbation of a natural system; in this case, providing a limiting nutrient to the entire community. The terrestrial equivalent would be to water an arid ecosystem. Based on our current understanding of succession in vegetation types across the rainfall gradient—from deserts to grassland to rainforest—we know what the long-term outcome of such an undertaking would be. By analogy, one could postulate the outcome of sustained fertilization of nutrient-rich SO waters by examining the species composition across the iron gradient from coastal and shelf to open ocean waters.

(c) Effect of neritic versus oceanic species on vertical carbon flux

The diatom flora of iron-rich continental margins differs significantly from that of the adjoining HNLC open ocean. The diatom genera, and in some cases species, typical of the Antarctic coastal and shelf environments are the same, or very similar to those that inhabit equivalent, more thoroughly studied environments in the northern ocean margins. These neritic species tend to be thin-shelled, small-celled, long-chained forms among which the spore-forming species of the spiny genus *Chaetoceros* are particularly prominent. They dominate the spring blooms of high latitudes and their aggregated chains are the major component of the mass sedimentation representing the annual peak in vertical flux that generally occurs after nutrient exhaustion (Smetacek 1985). Many of these coastal species (including *Chaetoceros* spp.) form compact resting spores under unfavourable growth conditions that, entrained within sinking diatom aggregates or zooplankton faecal pellets, settle out on the sediment surface and, in shallow regions, provide the seed stock for next year's bloom (Smetacek 1985). Such blooms are also typical for the shelves of Antarctica and Sub-Antarctic islands, where peak annual flux also occurs in their aftermath (Wefer 1989; Blain *et al.* 2007; Salter *et al.* 2007). However, the factor triggering mass flux, invariably

nitrate or silicate exhaustion around the northern Atlantic, will be different because macronutrients only rarely reach limiting concentrations in the entire SO. The studies carried out on the shelves of the islands of Kerguelen and Crozet have shown that iron plays the same role in terminating blooms here as do the macronutrients in northern waters with the same consequences for the biological carbon pump (Blain *et al.* 2007; Salter *et al.* 2007).

These typical coastal species extend oceanward in the productive plume of water downstream of the Antarctic Peninsula that extends across the open southwestern Atlantic Sector of the SO beyond South Georgia to approximately 30° W (Hart 1942). The higher productivity of this region during the spring, reflected in satellite images of chlorophyll, is apparently due to seaward entrainment of iron-rich winter water, emanating from contact with the convoluted shelf, land runoff and upwelling along the continental margin, possibly augmented by Patagonian dust. The dominance of *Chaetoceros* spores, representative of typically coastal species in the diatom assemblage of the underlying deep-sea sediments (Abelmann *et al.* 2006), also indicates that this coastal flora is advected seaward with the iron-rich waters. During the Last Glacial Maximum the zone dominated by these *Chaetoceros* spores extended much further across the southern Atlantic, coinciding with higher iron content of the sediment than during the Holocene, indicating that this coastal flora could be maintained over the deep ocean given an adequate supply of iron. Because the compact spores have evolved tough, grazer-resistant silica shells, their organic contents are more likely to survive breakdown during sinking and be buried in the sediments than in the case of vegetative cells.

We suggest that iron fertilization of the phytoplankton community of the SW Atlantic Sector will result in deeper drawdown and greater burial of organic matter, accompanied by less loss of silica, than in other regions of the ACC. Indeed, we intend testing this hypothesis in an iron fertilization experiment LOHAFEX (Loha is Hindi for iron) to be carried out jointly by India and Germany in the austral summer of 2009. We have selected the post-spring period and a region of quasi-stable eddies north of South Georgia for our experiment to test whether iron fertilization leads to revival of the coastal assemblage. Thus, during the experiment SEEDS in the NW Pacific a massive bloom of the typically coastal, spore-forming species *Chaetoceros debilis* was induced in HNLC waters. Unfortunately, the ship had to leave just as the bloom peaked, so its fate could not be determined (Tsuda *et al.* 2003). In a subsequent experiment (SEEDS-II) carried out under the same environmental conditions, a bloom did not develop, although the phytoplankton assemblage responded to iron addition by increasing photosynthetic efficiency (Suzuki *et al.* 2006). The lack of biomass accumulation was attributed to heavier grazing pressure (Tsuda *et al.* 2006), although the absence of an adequate seeding stock of *C. debilis* might have played a more decisive role. *C. debilis* also exhibited very high growth rates during EisenEx, but the initial seed stock was too small to contribute significantly to bloom biomass during the three weeks of the experiment (Assmy *et al.* 2007). Clearly, there are a number of hypotheses pertaining to the relative roles of growth and mortality environments (bottom-up and top-down factors, respectively) in selecting species dominance in phytoplankton blooms (Smetacek *et al.* 2004; Poulton *et al.* 2007) that can be tested in longer term OIF experiments.

(*d*) *Impact of grazing on iron-induced blooms*

All SO OIF experiments were carried out outside the region inhabited by Antarctic krill (*Euphausia superba*) that forms the food base of the Antarctic fauna: whales; seals; and penguins. The zooplankton of HNLC regions is dominated by salps (large, watery, barrel-shaped organisms that filter particles indiscriminately from water pumped through their gills) and copepods which, as the experiments demonstrate, were unable to prevent diatom biomass from accumulating. The situation might be different in the more productive regions around the continental margin frequented by krill; in particular, the SW Sector of the Atlantic reported to harbour more than 60 per cent of the entire population (Atkinson *et al.* 2004). Krill feed voraciously on diatom blooms, macerating the shells in gastric mills, and producing copious amounts of faecal matter in the form of loose strings with potentially high sinking rates. However, the friable faeces are also recycled in the surface layer (González 1992), so it has yet to be established whether krill grazing enhances carbon export relative to the flux of aggregated algal chains and phytodetritus from a senescent, ungrazed, diatom bloom. Krill roams its feeding grounds in compact swarms grazing down local diatom blooms and moving on in search of others (Smetacek *et al.* 1990). It has been recently shown that krill release substantial amounts of iron to their environment (Tovar-Sanchez *et al.* 2007), possibly leaching out from faecal material, in which case their grazing should lead to recycling iron and enable the bloom to recuperate after their departure. OIF experiments carried out in the krill habitat provide the ideal conditions to study the mechanisms running the biological carbon pump under natural conditions.

Longer term experiments will be required to follow the effect of OIF on zooplankton stocks. The experiments EisenEx and EIFEX significantly enhanced grazing and reproduction rates of the copepods (Jansen *et al.* 2006; Henjes *et al.* 2007) and it is likely that krill will respond in a similar manner. Following decimation of their major consumers, the great whales, krill stocks, instead of increasing (Laws 1977), have actually decreased. A statistical analysis of all net catches carried out in the former whaling grounds in the SW Atlantic Sector indicates an ongoing declining trend, with current stock size less than 20 per cent of that in the 1970s (Atkinson *et al.* 2004). Salps, an indicator of HNLC waters, have increased concomitantly, which is a sign of decreasing productivity (Smetacek 2007). It follows that the ongoing krill decline, which will seriously jeopardize recovery of the whale populations, might be reversed by larger scale OIF in the SW Atlantic. This hypothesis could be tested with a series of large-scale experiments carried out along the melting sea-ice edge of the Weddell-Scotia Confluence in austral spring.

7. Concluding remarks

The decision to carry out large-scale OIF should be based on a comprehensive assessment of the long- and short-term as well as local and global effects derived from experiments and models, hence taken by an international body, preferably an agency of the UN specifically established for the purpose. This science-oriented body would subsequently manage and monitor larger scale OIF whether carried out by itself (analogous to deployment of experts by the well-known

International Atomic Energy Agency, IAEA of the UN) or by private companies under contract. OIF can be opened to the carbon credit market only if such an independent body allots a specific carbon quota per tonne of iron added in a specific season and region. For reasons dealt with below, inherent uncertainties are likely to prevent the scientific community from ever being in a position to allot fixed quotas for the SO. Indeed, we feel it is highly unlikely that a free-for-all carbon market could ever take over the SO as feared by many scientists (Chisholm *et al.* 2001) owing to the verification problem. It is up to the scientific community to exercise tight control over any large-scale OIF operation by generating the knowledge required to assess its effects. Statements calling for more experiments have been made by several scientific and other international bodies (Buesseler *et al.* 2008).

We have outlined hypothetical differences between open ACC and land-influenced waters above; another region where a very different type of phytoplankton assemblage is present is the silicon-limited band of the ACC north of the Polar Front, in particular the regions where Antarctic Intermediate Water is formed. The SOFEX north patch, carried out in low-silicon waters, induced a bloom of thin-shelled pennate diatoms followed by significant enhancement of vertical flux (Bishop *et al.* 2004; Coale *et al.* 2004). However, in addition to thin-shelled diatoms, haptophyte flagellates known to produce copious quantities of DMSP, in particular the colonial species *Phaeocystis* and the calcifying coccolithophorids, also dominate the phytoplankton of this region (Seeyave *et al.* 2007; Lampitt *et al.* in press). If OIF stimulates growth of coccolithophorids then pCO_2 decrease caused by the uptake and export of organic carbon will be offset by the increase resulting from $CaCO_3$ formation that reduces the alkalinity as well as the pH of seawater.

Experiments in this area would shed light on the much debated factors, selecting for diatom or haptophyte dominance of the SO phytoplankton blooms (Smetacek *et al.* 2004). Thus, *Phaeocystis* blooms are recurrent in the Ross Sea but not in the Atlantic Sector and it cannot be excluded that sustained fertilization could lead to sustained blooming of this species, which does not appear to either provide high-quality food to zooplankton or contribute as efficiently to vertical flux as do diatoms. The toxic algal blooms reported from coastal waters around the world are unlikely to occur in the SO, although it cannot be excluded that toxic species of diatoms (*Pseudo-nitzschia* spp.), not currently present, may appear in the future. These possibilities underline the need to first carry out experiments but also, if they prove successful, to monitor carefully the effects of any large-scale OIF continuously and stop fertilization as needed.

Prolonged OIF will certainly have an effect on the zooplankton and possibly also on their predator populations. The latter are not a prominent feature of the HNLC ACC (Smetacek *et al.* 2004), so it is impossible to predict which groups, from jellies to mesopelagic fish and squid and even the copepod feeding, endangered Southern Right Whales, might profit from their population build-up. It will also be necessary to follow the effects of sustained fertilization on the mesopelagic community of copepods and radiolarians because, if their population density increases over time, they will intercept an increasingly larger proportion of the deep sinking flux. In such a case, it would be advisable to interrupt OIF for appropriate periods. It would also be necessary to monitor closely oxygen concentrations in the water column and sediments underlying OIF regions and halt operations before oxygen depletion occurs.

Even under the best possible conditions, OIF will have only a limited effect on the rate at which atmospheric CO_2 is projected to rise, but the amount involved is too large to be discounted; in short, we cannot afford not to thoroughly investigate the potential of this technique. A further benefit accruing from large-scale experiments is the attention they draw from the media, eager to report new developments in the global struggle, now in its infancy, to meet the challenge of global warming. The case for and against OIF can be used as a platform to educate the public on the workings of the global carbon cycle and the anthropogenic impact on it by providing a perspective on the quantities involved. OIF experiments would also serve as an ideal training ground for the next generation of ocean scientists faced with the challenge of coping with ongoing climate change in a global context.

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