The Role of Marine Biota in the Functioning of the Biosphere

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THE ROLE OF MARINE BIOTA IN THE CO_2 BALANCE OF THE OCEAN-ATMOSPHERE SYSTEM

by

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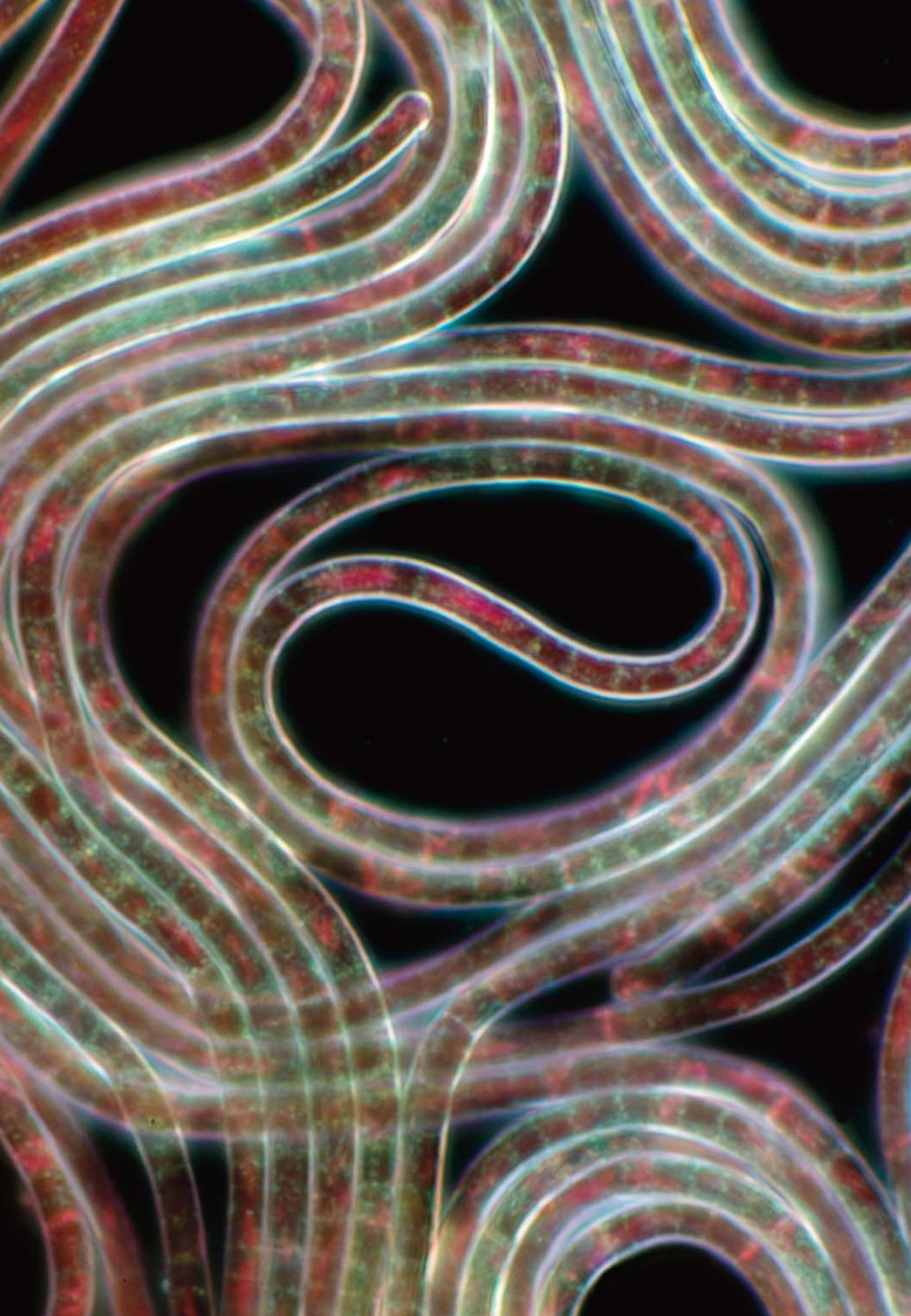

CHAPTER 4

THE ROLE OF MARINE BIOTA IN THE CO_2 BALANCE OF THE OCEAN-ATMOSPHERE SYSTEM

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THE OCEAN CARBON SYSTEM IS SUFFICIENTLY close to linear in its behavior that it is possible to consider it as consisting of two almost independent components due to: 1) the anthropogenic perturbation resulting from CO_2 injection into the atmosphere by human land use changes, the burning of fossil fuels, and a minor input resulting from cement production; and 2) the "natural" carbon cycle that was in place prior to the "Anthropocene" (cf. Crutzen and Stoermer 2000, for a definition), and which is generally assumed to have remained unchanged since then (although see, for example, Le Quéré et al. 2007, for evidence of recent relatively modest changes). This paper provides an overview of the natural carbon cycle and how it influences the air-sea balance of CO_2, with a review of recent ideas on how the natural carbon cycle might be modified to enhance CO_2 removal from the atmosphere as a form of carbon mitigation.

The paper is divided into four sections. The first provides a brief overview of the natural carbon cycle based largely on Sarmiento and Gruber (2006), which the reader is encouraged to consult for a more detailed discussion. The

◂ **Photo 4.1: *Oscillatoria animalis* cyanobacteria, dark field light micrograph.** The genus name for this cyanobacterium comes from the movement it makes as it orientates itself to the brightest light source available, from which it derives energy by photosynthesis.

major focus of this overview is on how biogeochemical processes in the ocean affect the air-sea balance of CO_2; the existence of anomalous regions of very high surface nutrient concentrations and surprisingly low biological activity in areas where the conditions would seem to be ideal for biology to flourish and nutrients to be completely consumed; and how these regions of anomalously high nutrient concentrations affect the air-sea balance of CO_2. The second section discusses the important role of iron limitation in helping to explain these anomalous high nutrient/low biological activity regions. The third and fourth sections turn to a discussion of model simulations of how relief of iron limitation in these regions would affect the air-sea CO_2 balance and the implications of this for carbon mitigation, respectively.

4.1. THE BIOLOGICAL PUMP AND AIR-SEA CO_2 BALANCE

When CO_2 dissolves in the ocean, a series of hydrolysis reactions ensue that added together have the following net effect on ocean carbon chemistry

$$CO_2 + H_2O + CO_3^{2-} \rightleftharpoons 2HCO_3^-$$

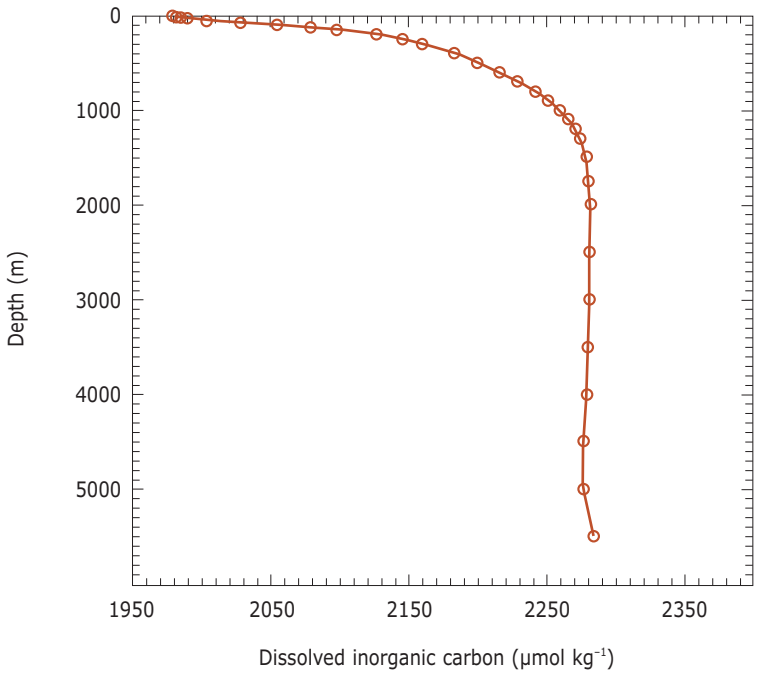
Given that inorganic carbon exists interchangeably as carbon dioxide, carbonate ion, or bicarbonate ion, we generally characterize the inorganic carbon content of the ocean as consisting of the sum of the three of these

$$DIC = CO_2 + HCO_3^- + CO_3^{2-}$$

where *DIC* is the *dissolved inorganic carbon*. On average, only about 0.5% of the *DIC* exists in the surface ocean as carbon dioxide, with 88.6% as bicarbonate ion and 10.9% as carbonate ion. This ability of the ocean carbon system to convert interchangeably between these three species, and the fact that the ocean chemistry is such as to permit the vast majority of *DIC* to exist in the carbonate and bicarbonate forms, is the principal reason why atmospheric CO_2 comprised only 1.5% of the combined atmosphere-ocean inventory of carbon prior to the beginning of the industrial revolution. For most other gases, such as oxygen, the proportions are roughly reversed due to the low solubility of most gases in seawater and the absence of a buffer effect such as that of the carbon system.

The global mean *DIC* concentration is 2,255 µmol kg^{-1}. However, figure 4.1 shows that *DIC* is not uniformly distributed, with *DIC* being about 300 µmol kg^{-1}

Figure 4.1: Vertical profile of horizontally averaged dissolved inorganic carbon in the ocean

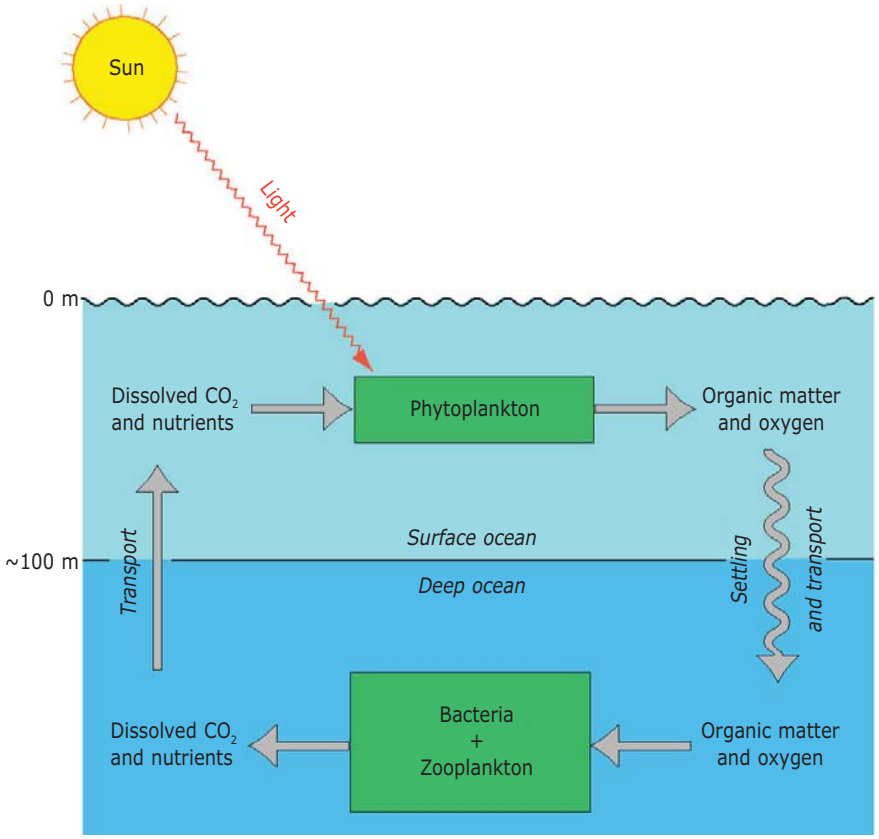


Source: Based on the GLODAP data set of Key et al. 2004.

higher at depth than at the surface. A little less than one-third of this surface to deep difference can be accounted for by the capacity of cold waters to hold more *DIC* than warm waters when brought into equilibrium with the atmosphere. The abyssal ocean is filled entirely with cold waters, whereas the surface waters are warmer on average due especially to the low latitudes. The vertical gradient in *DIC* that results from this solubility difference is referred to as the *solubility pump*.

The remaining two-thirds of the vertical *DIC* gradient is due to the *biological pump* illustrated in figure 4.2. This consists of four components: 1) the formation of organic matter and $CaCO_3$ from dissolved inorganic carbon and nutrients by photosynthesis in the surface ocean, 2) the export into the deep ocean of some of this $CaCO_3$ in particulate form, and some of the organic matter in both particulate and dissolved forms (about 80% of the organic matter is recycled within the surface ocean), 3) the conversion of the organic matter and $CaCO_3$ back into the dissolved inorganic form in the deep ocean by dissolution of $CaCO_3$, and by bacterial and zooplankton pro-

Figure 4.2: The great biogeochemical loop. An illustration of the biological pump described in the text.



Source: Modified by Gruber (personal communication) from Sarmiento and Gruber 2006.

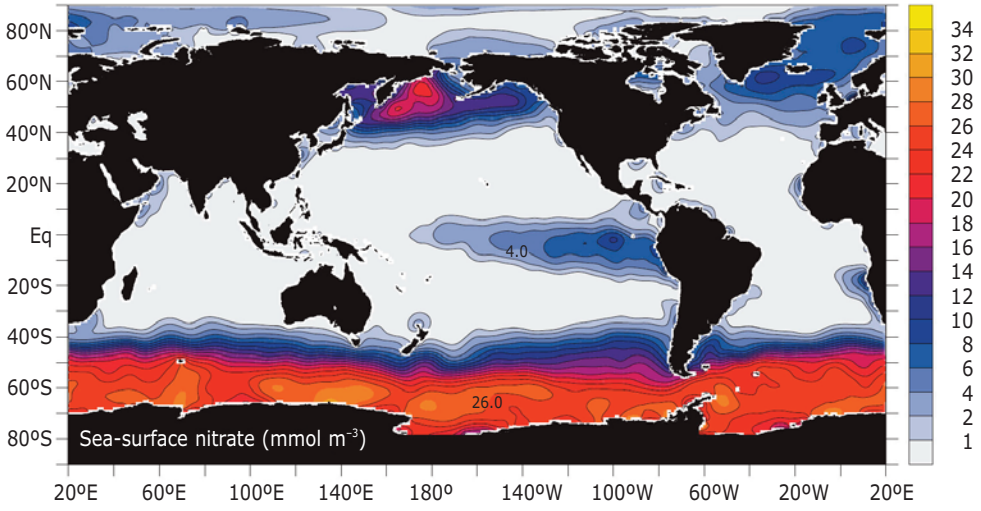
cessing of organic matter, a process referred to as *remineralization*, and 4) the closing of the loop by the upward transport of inorganic carbon and nutrients by the ocean circulation and mixing. The recycling of carbon and nutrients by this "great biogeochemical loop" is almost 100% efficient, with only a tiny leakage of carbon into the sediments and to the atmosphere by gas exchange, balanced by a river input resulting from weathering reactions and organic matter formation on land (e.g., Sarmiento and Sundquist 1992). While the loop is indeed almost closed in the ocean, the enhancement of the deep ocean *DIC* concentration by the biological pump (as well as the solubility pump) lowers the CO_2 content of the atmosphere relative to a world with the same total inventory of carbon and no biological pump. Simplified model studies show that shutting down the biological pump

would release an amount of CO_2 to the atmosphere sufficient to increase its concentration from its pre-industrial value of 280 ppm to something in excess of 450 ppm. Marine biota thus play an important role in establishing the concentration of atmospheric carbon dioxide and therefore in the climate of the planet.

The impact of the marine biota may vary both temporally and spatially. In the modern ocean the biological pump is not working at full efficiency, as measured here by the effectiveness of phytoplankton in depleting nitrate from the surface of the ocean. Nitrate is the limiting nutrient for biological production over much of the ocean, and thus tends to be very close to depleted (map 4.1). However, there are three principal regions of the ocean, in the North Pacific, Equatorial Pacific, and Southern Ocean, where nitrate is never depleted, even in the summer when there is plenty of light. These regions are anomalous not only in having high nutrients, but also in having a low ratio of chlorophyll to nutrients, and are often referred to as High Nutrient/Low Chlorophyll or HNLC regions.

The North Atlantic also has high nitrate concentrations in the annual average, but here the nitrate is depleted in the summer time so it does not fit the definition of a classic HNLC region. In the following section we discuss how iron limitation can explain why nitrate is not depleted in the HNLC regions.

Map 4.1: Annual mean nitrate concentration at the surface of the ocean



Source: Sarmiento and Gruber 2006, based on the *World Ocean Atlas 2001* (Conkright et al. 2002).

Table 4.1: Results of regional nutrient depletion simulations in several models: in the KVHISOUTH ocean circulation and biogeochemistry model described by Gnanadesikan et al. (2002), in the new ocean biogeochemistry (Dunne et al. in prep; and Appendix by Dunne et al. in Sarmiento et al. 2009) and general circulation model described by Sarmiento et al. (2010).

a: KVHISOUTH, diagnostic biology with interactive atmosphere

Region of nutrient depletion	Atmospheric CO_2 uptake (Pg C)		
	50 years	100 years	2000 years
North Pacific (30°N to 67°N)	6.2	7.3	6.7
North Atlantic (30°N to 80°N)	7.2	10.8	32.0
Tropics (18°S to 18°N)	8.3	9.7	7.7
Southern Ocean (90°S to 30°S)	67.6	83.1	146.1
Global	91.2	110.6	178.4

b: New model (prognostic biology) with interactive atmosphere

Region of iron fertilization	Net atmospheric CO_2 uptake (Pg C)	
	50 years	100 years
North Pacific (30°N to 67°N)	5.0	6.7
North Atlantic (30°N to 80°N)	(0.8)	(1.1)
Tropics (18°S to 18°N)	(13.2)	(20.2)
Southern Ocean (90°S to 30°S)	58.9	74.9
Global	71.6	89.6

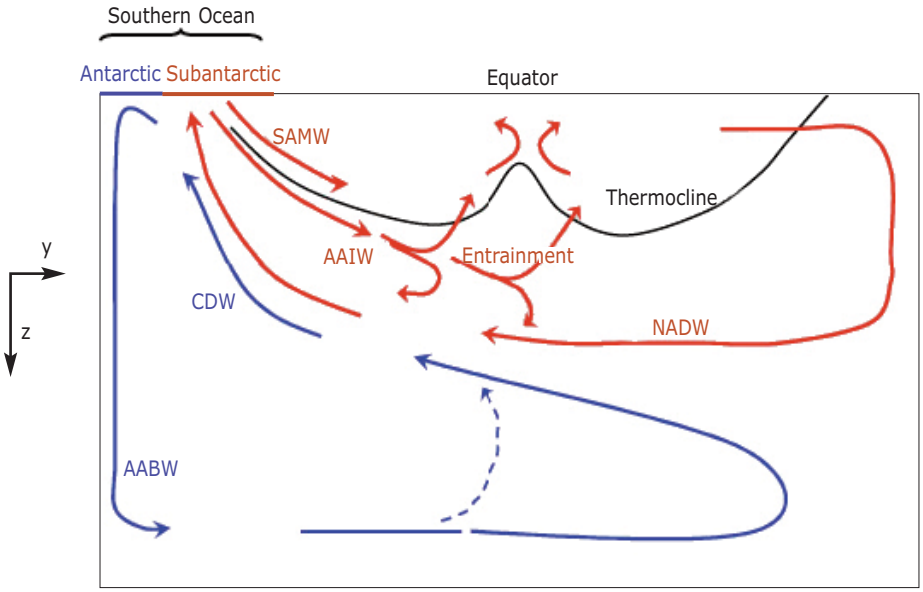
c: New model (prognostic biology) with fixed atmosphere

Region of iron fertilization	Atmospheric CO_2 uptake (Pg C)	
	50 years	100 years
North Pacific (30°N to 67°N)	8.5	13.7
North Atlantic (30°N to 80°N)	(1.4)	(2.3)
Tropics (18°S to 18°N)	(21.9)	(40.1)
Southern Ocean (90°S to 30°S)	103.8	159.2
Global	127.6	191.6

See text for discussion of these results and for the difference between simulations done with an interactive atmosphere versus those done with a fixed atmosphere. The results in parentheses in tables 4.1b and 4.1c are suspect, as discussed in the text.

Model perturbation studies can be used to isolate the impacts of the HNLC regions on the global carbon balance. Table 4.1a shows an ocean general circulation model study of what would happen in a model with diagnostic biology, that is, one in which surface biological processes are simulated by forcing model predicted surface nutrients towards the observed nutrient distribution, with carbon linked to the nutrients by a stoichiometric ratio, if a way could be found to overcome the barriers to nutrient depletion in these regions such that the nutrient concentrations were drawn down to 0 throughout the year. Consistent with earlier work discussed, for example, in Sarmiento and Gruber (2006), we find that neither the North Pacific nor the tropical region (we depleted nutrients over the entire tropical ocean, not just the Pacific HNLC region), nor the North Atlantic is able to remove a significant amount of CO_2 from the atmosphere. By contrast, nutrient depletion in the Southern Ocean is able to remove 39 ppm of CO_2 over 100 years, which is more than one-third of the increase in CO_2 of almost 110 ppm that has occurred since the beginning of the industrial revolution. Note that this is without the additional uptake due to the ocean alkalinity feedback effect that occurs on millennial time scales (cf. Archer et al. 2000), and which is beyond the scope of this paper.

Figure 4.3: A schematic of the global ocean conveyor belt circulation, consisting of an upper (red) loop and a lower (blue) loop as described in the text.



A particularly interesting aspect of the Southern Ocean carbon cycle (discovered by Marinov et al. 2006) is that there is a biogeochemical divide, north of which nutrient depletion has only a minimal effect on atmospheric CO_2, much like the North Pacific and tropics, with most of the atmospheric CO_2 drawdown capacity occurring south of this divide nearer to the Antarctic continent (figure 4.4a and table 4.2). This divide is associated with the surface manifestation of the upper and lower meridional overturning cells illustrated schematically in figure 4.3. As can be seen from the distribution of radiocarbon (cf. Gnanadesikan et al. 2007), the Southern Ocean is the location where the ocean's deepest waters are brought to the ocean surface. Some of these waters move northward into regions where the Subantarctic Mode and Antarctic Intermediate Waters form, sink down to the base of the main thermocline and flow even further northward. Eventually, these waters feed the sinking of deep waters in the North Atlantic Ocean. This upper meridional overturning loop is the main conduit for the return flow of biological pump nutrients from the

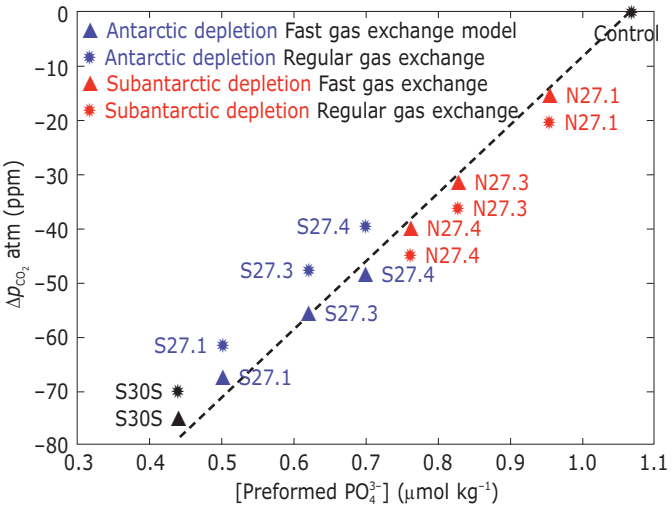
Table 4.2: Impacts of seasonality on Southern Ocean nutrient depletion simulations performed with the so-called LL model. The nutrient depletion is performed in different regions of the Southern Ocean as indicated in the top line. The seasons are defined as June, July, August for winter, and December, January and February for the summer. Three results are shown for each season, the first being the change in atmospheric p_{CO_2}, $\Delta p_{CO_{2atm}}$ in ppm; then the physical chemical efficiency defined in equation 4.4 (p. 83) but here calculated with respect to changed production only in the region of fertilization rather than in the world as a whole, $e_{phys\text{-}chem,S30°S} = \Delta p_{CO_{2atm}}/\Delta \mathrm{Prod}_{S30°S}$ in units of ppm (Pg C yr^{-1})$^{-1}$; and finally the change in production north of 30°S relative to the removal of CO_2 from the atmosphere, $\Delta \mathrm{Prod}_{N30°S}/\Delta p_{CO_{2atm}}$ in (Pg C yr^{-1}) ppm^{-1}.

Region of nutrient depletion		South of 30°S	South of σ_θ 27.1	South of σ_θ 27.6	North of σ_θ 27.1
Winter depletion	$\Delta p_{CO_{2atm}}$	48	42	18	7.9
	$e_{phys\text{-}chem,S30°S}$	-13	-38	-48	-2.6
	$\Delta \mathrm{Prod}_{N30°S}/\Delta p_{CO_{2atm}}$	0.068	0.048	0.0012	0.17
Summer depletion	$\Delta p_{CO_{2atm}}$	45	39	17	6.9
	$e_{phys\text{-}chem,S30°S}$	-16	-52	-80	-3.4
	$\Delta \mathrm{Prod}_{N30°S}/\Delta p_{CO_{2atm}}$	0.078	0.054	0.0019	0.22
Annual depletion	$\Delta p_{CO_{2atm}}$	73	66	32	16.8
	$e_{phys\text{-}chem,S30°S}$	-13	-26	-45	-3.28
	$\Delta \mathrm{Prod}_{N30°S}/\Delta p_{CO_{2atm}}$	0.068	0.054	0.0017	0.19

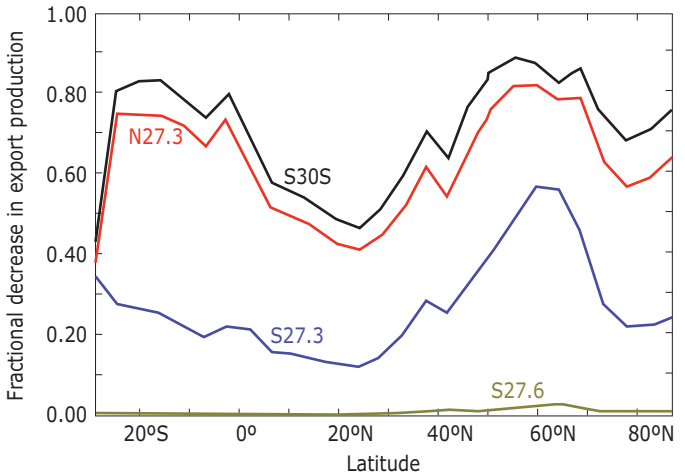
Source: Results are from Marinov 2005.

Figure 4.4: Oceanic mechanisms for modifying atmospheric p_{co_2} and global production in the Princeton GCM. Results of experiments where surface nutrients are depleted south of 30ºS (experiment S30S), and south and north of the outcrops of σ_θ = 27.1 (experiments S27.1, N27.1), σ_θ = 27.3 (S27.3, S27.3), σ_θ = 27.4 (S27.4, N27.4), respectively. Experiments S27.4, S27.3, S27.1 (in blue) roughly represent depletion in the Antarctic; experiments N27.4, N27.3, N27.1 (in red) roughly represent nutrient depletion in the Subantarctic (see figure 4.3). **a)** Surface nutrient depletion results in a decrease in globally averaged preformed PO_4 (*x*-axis in the figure) and consequently a drawdown in atmospheric pCO_2 (*y*-axis in the figure) relative to the undepleted "Control" simulation (top right corner, black star). For all simulations, CO_2 drawdown is similar in our regular gas exchange (stars) and fast gas exchange (triangles) models. The important observation is that Antarctic nutrient depletion (blue triangles and stars) result in a larger decrease in preformed nutrients and stronger atmospheric CO_2 drawdown than Subantarctic depletion (red triangles and stars). **b)** Fractional decrease in export production (*y*-axis) versus latitude, following nutrient depletion experiments. Depleting nutrients in the Subantarctic (experiment N27.3) has much more impact on global export production north of 20ºS than depleting them in the Antarctic (experiment S27.3).

a)



b)



Source: Marinov et al. 2006.

deep ocean to the upper ocean, single-handedly accounting for about three-quarters of the biological production north of 30°S as shown by Sarmiento et al. (2004) and in figure 4.4b.

As shown in table 4.2, the change in production north of 30°S relative to the removal of CO_2 from the atmosphere, $\Delta Prod_{N30°S}/\Delta p_{CO_{2atm}}$, is 3.5 to 4 times higher for nutrient depletion south of 30°S and north of the surface outcrop of σ_θ = 27.1, than it is for regions to the south of this outcrop, with an even larger contrast for fertilization south of the surface outcrop of σ_θ = 27.6. An important reason why nutrient depletion in the surface outcrops of the upper loop (i.e., the Subantarctic region in figure 4.3) does not have much of an impact on atmospheric CO_2 is because most of these nutrients and the associated biological pump carbon are eventually removed from the surface by the efficient biological pump in lower latitudes. Removing the nutrients in the Southern Ocean portion of this loop only accelerates a process that eventually occurs anyway and thus does not have much of an impact on the air-sea balance of carbon. By contrast, the upwelling waters that move southward in the Southern Ocean (i.e., the Antarctic region in figure 4.3) find themselves in an environment where nutrients are not utilized efficiently. This allows a decoupling of carbon from nutrients, with carbon dioxide escaping to the atmosphere while nutrients are reinjected into the abyssal ocean. Depletion of nutrients in the region south of the biogeochemical divide is what accounts for most of the response of the atmospheric CO_2 to Southern Ocean nutrient depletion (figure 4.4a and table 4.2). Thus, by far the greatest remaining capacity for additional removal of CO_2 from the atmosphere in the present ocean south of the biogeochemical divide is in the high latitudes of the Southern Ocean where Antarctic Bottom Water and lower Circumpolar Deep Water are formed. The processes that prevent nutrient removal from occurring in this region are the subject of the next section of this paper.

The large scale macronutrient manipulation simulations demonstrate that the air-sea CO_2 balance is best understood by analyzing the fraction of total nutrients in the ocean that is remineralized, and thus associated with carbon, versus the fraction that is "preformed," i.e. injected into the deep ocean without being associated with carbon (Ito and Follows 2005; Marinov et al. 2008a, 2008b). The key insight is that the remineralized nutrient pool can be thought of as the difference between the total nutrient pool and the preformed pool. The total accumulation of dissolved inorganic carbon in the ocean due to the remineralization process (defined below as the soft-tissue

Ocean Carbon Storage or OCS_{soft}) is stoichiometrically related to the remineralized nutrient pool:

$$OCS_{soft} = r_{C:P} \cdot \overline{PO_{4remin}} \cdot V_{oc} = r_{C:P} \cdot \left(\overline{PO_4} - \overline{PO_{4pref}}\right) \cdot V_{oc} \qquad (4.1)$$

where V_{oc} is the ocean volume, PO_4, PO_{4remin}, PO_{4pref} are the total, remineralized and preformed ocean phosphate and an overbar denotes global mean. Changes in biological cycling or circulation that reduce the preformed pool will thus increase the remineralized pool and draw down atmospheric carbon dioxide. Assuming surface ocean CO_2 equilibrates instantaneously with the atmosphere and disregarding the solubility pump, Marinov et al. (2008a) showed that atmospheric p_{CO_2} decreases exponentially with the remineralized pool:

$$p_{CO_{2a}} = c \cdot e^{-\frac{OCS_{soft}}{a_1}} + c^2 \cdot \frac{a_2}{a_1} e^{-\frac{2\,OCS_{soft}}{a_1}} + c^3 \cdot \frac{3 \cdot a_2^2}{2 \cdot a_1^2} e^{-\frac{3\,OCS_{soft}}{a_1}} + \ldots \qquad (4.2)$$

where a_1 and a_2 are coefficients related to buffer chemistry and c is a constant of integration.

Thus, because the region to the south of the biogeochemical divide is the dominant source of preformed nutrients to the deep ocean, increasing biological activity in this region will have a disproportionate impact on the oceanic preformed nutrient inventory and the biggest effect on atmospheric carbon dioxide. However, changes in circulation can also change the preformed nutrient pool. For example, reducing the contribution of high-preformed nutrient Southern Ocean deep water relative to lower preformed nutrient North Atlantic Deep Water will also alter the total preformed nutrient content of the ocean and thus change the atmospheric carbon dioxide. It is this ability to capture the impacts of changing both circulation and biological activity that motivates analysis of the biological pump in terms of preformed nutrients.

Marinov et al. (2008b) examined the biological pump in a suite of models with different circulation patterns, but in which the HNLC regions were constrained to have their modern nutrient concentrations. They found that a circulation scheme in which vertical mixing is strong can result in both higher biological productivity and higher atmospheric carbon dioxide com-

pared to a lower-mixing control. This apparent paradox is resolved by the finding that the higher mixing model injects relatively more deep water via the Southern Ocean and therefore has higher preformed nutrients in the deep than the control model. Higher preformed nutrients imply less remineralized nutrient in the ocean and, according to Equation 4.2, higher atmospheric p_{CO_2}. Thus, contrary to conventional wisdom, atmospheric p_{CO_2} can decrease, while surface nutrients show minimal change and export production decreases.

4.2. THE ROLE OF IRON IN LIMITING THE BIOLOGICAL PUMP

The principal hypothesis for what prevents nutrients from being drawn down in the HNLC regions is that these regions are iron limited, an idea for which observational support first began to appear in a series of papers published by John Martin in the late 1980's and early 1990's (e.g., Martin and Fitzwater 1988; Martin et al. 1990a; Martin 1992). Iron is an important component of electron transport proteins involved in photosynthesis and respiration, as well as in enzymes required to fix nitrogen and utilize nitrate and nitrite. The evidence in support of the iron limitation hypothesis has grown over time based principally on a wide range of mesoscale iron manipulation experiments such as those described by Martin et al. (1994), Coale et al. (1996), Boyd et al. (2000), Gervais et al. (2002), Tsuda et al. (2003), Boyd et al. (2004), Coale et al. (2004), and Hoffmann et al. (2006); reviews by de Baar et al. (2005) and Boyd (2007), and based on studies of natural iron fertilization at the Kerguelen plateau and Crozet Island in the Southern Ocean by Blain et al. (2007) and Pollard et al. (2009), respectively. This brief review of the principal findings of these studies closely follows the recent paper of Sarmiento et al. (2009).

These experimental manipulations and observational studies clearly demonstrate that iron fertilization results in a drawdown of nitrate (cf. summary table given in Sarmiento and Gruber 2006), but what is their impact on carbon? As in Sarmiento et al. (2009), we find it useful in analyzing the impact of the iron manipulation experiments on the carbon distribution to define the overall efficiency of iron fertilization in removing CO_2 from the atmosphere as the cumulative perturbation atmospheric CO_2 uptake $\Delta\Phi^{CO_2}_{air\text{-}sea}$ divided by the cumulative iron addition $\Delta\Phi^{Fe}_{fertilization}$, i.e.,

$$R^{\mathrm{C:Fe}}_{overall} = \frac{\Delta\Phi^{\mathrm{CO_2}}_{air\text{-}sea}}{\Delta\Phi^{\mathrm{Fe}}_{fertilization}} \tag{4.3}$$

where we define Φ (units of mol) as the cumulative area and time integral of a flux (f) of tracers such as Fe, organic matter, $CaCO_3$ or CO_2 across a depth level or the air-sea interface:

$$\Phi = \int_0^{\tau}\iint f \mathrm{d}x\mathrm{d}y$$

The delta symbols refer to the difference between the patch iron fertilization scenario and the control scenario with no fertilization.

We further separate the overall response function into a *physical-chemical efficiency*, $e_{phys\text{-}chem}$, defined as the ratio of the uptake of CO_2 from the atmosphere, $\Delta\Phi^{\mathrm{CO_2}}_{air\text{-}sea}$, to the cumulative perturbation export of carbon from the surface ocean, $\Delta\Phi^{\mathrm{Org\ C\ \&\ CaCO_3}}_{export}$, that results from iron fertilization; and a *biogeochemical response function* $R^{\mathrm{C:Fe}}_{iron\ utilizatión}$ defined as the ratio of $\Delta\Phi^{\mathrm{Org\ C\ \&\ CaCO_3}}_{export}$ to $\Delta\Phi^{\mathrm{Fe}}_{fertilization}$. In equation form, we have that:

$$\begin{aligned} R^{\mathrm{C:Fe}}_{overall} &= e_{phys\text{-}chem} \cdot R^{\mathrm{C:Fe}}_{iron\ utilizatión}, \text{ where} \\ e_{phys\text{-}chem} &= \frac{\Delta\Phi^{\mathrm{CO_2}}_{air\text{-}sea}}{\Delta\Phi^{\mathrm{Org\ C\ \&\ CaCO_3}}_{export}}, \text{ and} \\ R^{\mathrm{C:Fe}}_{iron\ utilizatión} &= \frac{\Delta\Phi^{\mathrm{Org\ C\ \&\ CaCO_3}}_{export}}{\Delta\Phi^{\mathrm{Fe}}_{fertilization}} \end{aligned} \tag{4.4}$$

(cf. Jin et al. 2008).

As noted in the summary by Sarmiento et al. (2009), from which the following review paragraphs are taken, the mesoscale iron enrichment experiments referred to above have shown that the drawdown in surface dissolved inorganic carbon (*DIC*) that results from a given iron addition occurs at an average ratio of $R^{\mathrm{C:Fe}}_{iron\ utilizatión}$ = 5,600 mol C to mol Fe added (de Baar et al. 2005). This is considerably smaller than the intracellular C:Fe ratios of ~20,000 to 500,000 typically observed in laboratory experiments with oceanic phytoplankton as summarized by Fung et al. (2000) and Sunda (2001), or than the mean C:Fe ratio

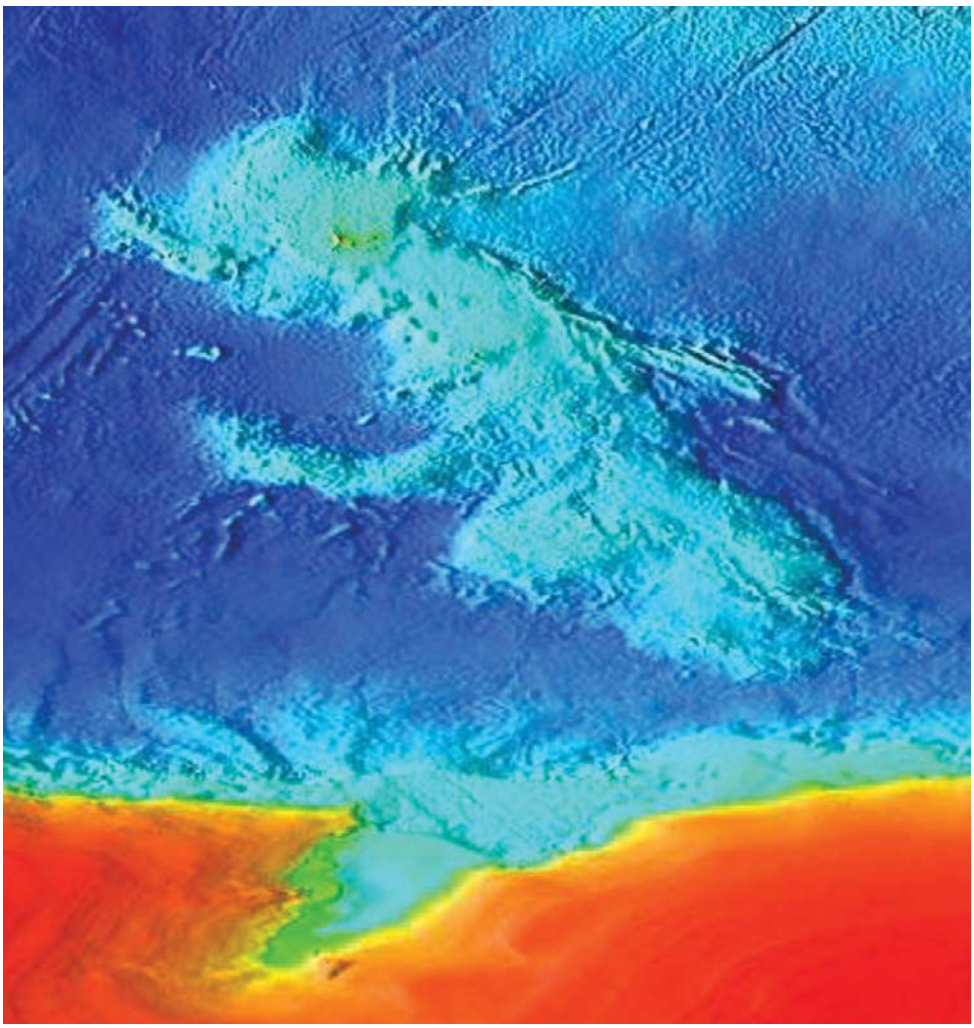
of 200,000 proposed by Johnson et al. (1997). This suggests that most of the iron that is being added to the ocean is not being utilized by phytoplankton, at least on the time-scale of the observations. In addition to this problem, there has been only partial success in demonstrating that *DIC* uptake by iron fertilization actually results in carbon export from the surface ocean. The limited observational period of most experiments seems a likely reason for the failure to observe a significant export flux in many cases (Buesseler et al. 2004; de Baar et al. 2005). For example, in one of the few successful observations of particle fluxes, Bishop et al. (2004) used autonomous floats with optical measurements of the "carbon flux index" to show a large flux of particulate organic carbon at the SOFeX northern patch site beginning only 25 to 45 days after iron addition was initiated. Based on their measurements, Bishop et al. (2004) estimated a C export to Fe added ratio of $R^{C:Fe}_{iron\ utilization}$ = 10,000 to 100,000, which is more consistent with what might be expected from the laboratory experiments.

The problems inherent in short term manipulation experiments have motivated a new series of observational studies at locations within HNLC regions where islands provide a local long-term source of iron. Such studies of natural iron fertilization at the Kerguelen plateau (map 4.2) and Crozet Island in the Southern Ocean have detected a large excess particulate organic carbon export in iron fertilized regions relative to that in adjacent non-fertilized regions using the ^{234}Th deficit method. The ratio of the excess C export to Fe supply is estimated to be $R^{C:Fe}_{iron\ utilization}$ = 70,000 ± 46,000 at Kerguelen at the time of observations by Blain et al. (2007). At Crozet, Pollard et al. (2009) found that the mean daily rates of carbon export were similar in the iron fertilized region and in the HNLC region after the chlorophyll peak. However, they calculated different bloom durations for each region by using ^{234}Th/opal ratios to close the silicate budget. The seasonal ratio of excess C export to Fe supply at Crozet was estimated to be 17,200 (5,400-60,400) at 100 m and 8,600 at 200 m. Estimates based on the seasonal *DIC* and Fe budgets at Kerguelen give a much higher seasonal mol C to mol Fe ratio of $R^{C:Fe}_{iron\ utilization}$ = 668,000. The reason for the large difference between the Kerguelen and Crozet seasonal estimates of $R^{C:Fe}_{iron\ utilization}$ is not understood (e.g., Pollard et al. 2009).

Despite the large uncertainties, the natural iron fertilization studies and some of the iron manipulation studies have clearly demonstrated that iron fertilization of HNLC regions should eventually give rise to an increased particle

export flux. What can be said about the physical-chemical efficiency $e_{phys\text{-}chem}$, i.e., the extent to which the resulting reduction in surface *DIC* will actually remove CO_2 from the atmosphere? The short time span of the iron manipulation experiments is problematic for verification of the impact of iron fertilization on the air-sea balance of CO_2. A typical air-sea e-folding equilibration time for a 40 m mixed layer is of the order of six months (cf., Sarmiento and Gruber 2006), as contrasted with the time scale of a few weeks of the experiments. Thus, the air-sea CO_2 flux estimated from the *DIC* deficit during the

Map 4.2: Topographical map of the Kerguelen plateau, a large underwater volcanic igneous province in the Southern Indian Ocean. The red patch below the plateau is the continent of Antarctica.



fertilization period is only a miniscule part of the carbon budget, an average of 8% of the *DIC* drawdown per de Baar et al. (2005).

The time scale of the natural iron fertilization studies is more suitable, though still not ideal. Estimates of air-sea CO_2 gas flux over a 75-day period during the Crozet Island experiment by Bakker et al. (2007) gave an average uptake of 700 ± 600 mmol m^{-2} inside the fertilized patch versus 240 ± 120 mmol m^{-2} outside the patch, for a net uptake of 460 ± 580 mmol m^{-2} due to the added iron. Pollard et al. (2009) give a particulate organic carbon (POC) export of 960 mmol m^{-2} in the patch versus 290 mmol m^{-2} outside for a net of 670 mmol m^{-2}, with no uncertainty reported. The air-sea CO_2 uptake in the Crozet iron fertilized region thus gives a physical-chemical efficiency of $e_{phys\text{-}chem}$ ~ 69%, but with quite a large uncertainty. Using the 90 day seasonal carbon flux estimates of Jouandet et al. (2008) of 5,400 ± 1,900 mmol m^{-2} inside the patch versus 1,700 ± 400 mmol m^{-2} outside the patch, and air-sea flux of 28 ± 24 mmol m^{-2} d^{-1} inside the patch and –2.7 ± 2.3 mmol m^{-2} d^{-1} outside the patch, 90 days/2 to account for the whole season, Sarmiento et al. (2009) calculate $e_{phys\text{-}chem}$ = 37%, again with a very large uncertainty. However, even the 75 and 90 day time periods over which the air-sea flux was estimated in the natural fertilization studies is insufficient to fully capture the equilibration of the surface *DIC* perturbation. More importantly, although such studies very likely capture a substantial fraction of the immediate response to iron fertilization, there are other longer term processes that modify the overall chemical-physical efficiency of the iron fertilization, such as the global backflux of CO_2 that results from reduction of atmospheric CO_2 (cf., Gnanadesikan et al. 2003; Oschlies, 2009; Sarmiento et al. 2009).

In conclusion, while the uncertainties are very large and the extent and solidity of the evidence varies from location to location, the experimental work does clearly show that adding iron to HNLC regions results in a rapid uptake of dissolved inorganic nutrients and carbon that is greater than in the surrounding unfertilized waters. It would be expected that such an enhancement of the uptake would result in an enhanced export of organic matter, but this has only been observed in those few cases where there was longer term monitoring. Finally, it is only in the natural iron fertilization studies where the time scale of the experiments has been long enough for meaningful observations of the impact of iron fertilization on the air-sea flux of CO_2 to be obtained (photo 4.2).

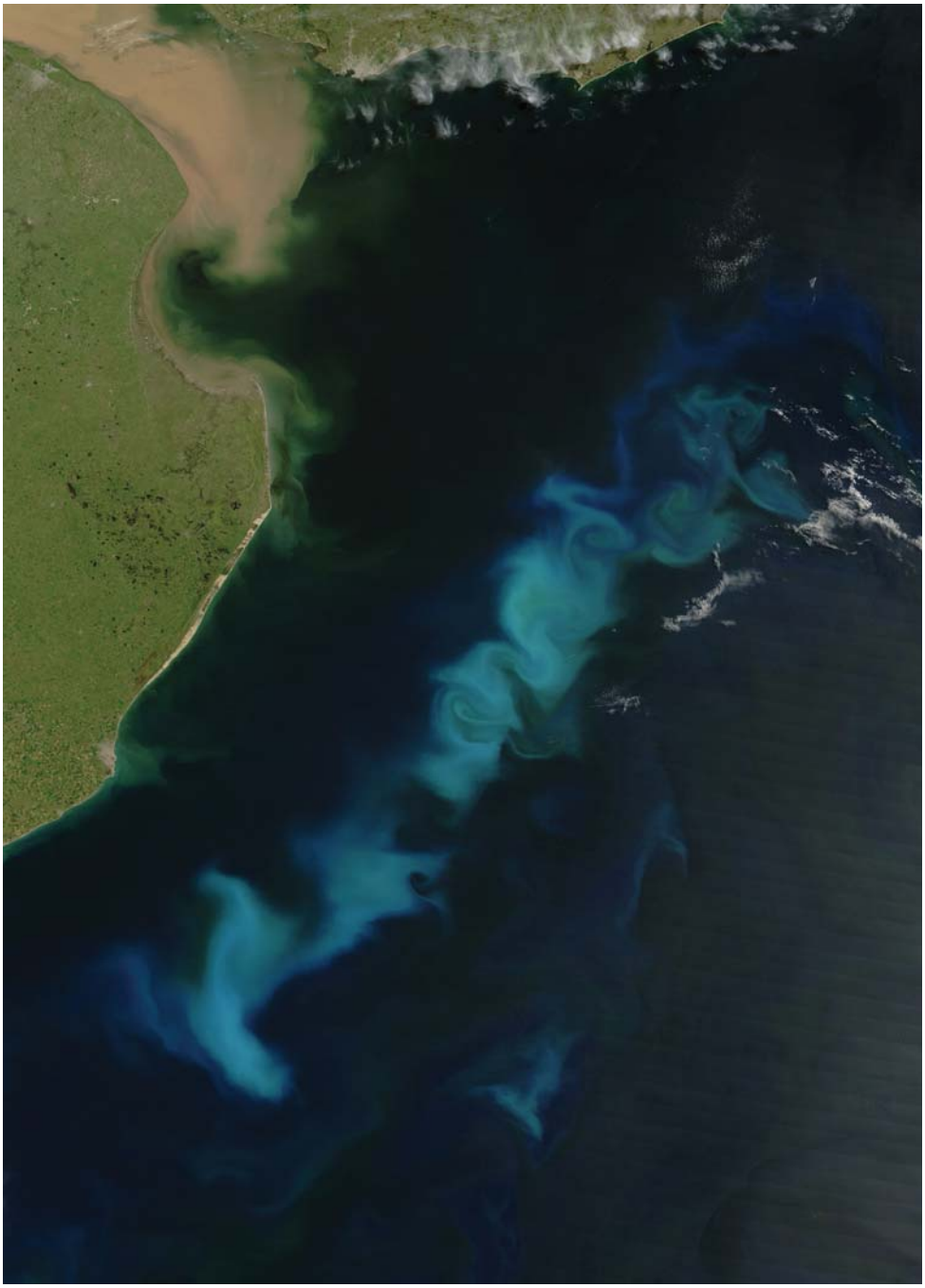


Photo 4.2: Phytoplankton bloom in the South Atlantic Ocean, off the coast of Argentina. Iron is a trace element necessary for photosynthesis, however it is highly insoluble in sea water and is often the limiting nutrient for phytoplankton growth. Large phytoplankton blooms can be created by supplying iron to iron-deficient ocean waters.

4.3. ENHANCEMENT OF OCEANIC CO_2 SEQUESTRATION BY IRON FERTILIZATION

The previous two sections demonstrated that the biological pump can exert a significant control over the air-sea balance of carbon dioxide and that the flux of iron to the ocean can change the biological pump. This section examines the link between these results. Such a connection was first made by Martin (1990) who noted that during the last ice age the delivery of iron-bearing dust to the oceans was much higher than at present and atmospheric carbon dioxide was much lower than at present. Discovered in ice core records (Barnola et al. 1983), lower atmospheric p_{CO_2} during glacial periods is challenging to explain because it is widely accepted that terrestrial vegetation held less carbon, and the ocean, though colder than at present, is unlikely to have been able to absorb all the additional carbon dioxide. Previous work by Knox and McElroy (1984), Sarmiento and Toggweiler (1984), and Siegenthaler and Wenk (1984) using box models had earlier noted that either an increase in high latitude production or a decrease in high latitude vertical exchange (either of which would result in a reduction in preformed nutrients) could easily explain such a drop; but the reason for increased production or decreased exchange had not been identified. An additional major impetus for study of the connection between iron and the ocean carbon inventory has been the carbon mitigation proposal first articulated by Martin et al. (1990a) and Martin et al. (1990b) to artificially fertilize the ocean with iron as a way of removing CO_2 from the atmosphere. In this section, we use a series of models to examine how large an impact on air-sea carbon partitioning could be associated with changes in iron supply.

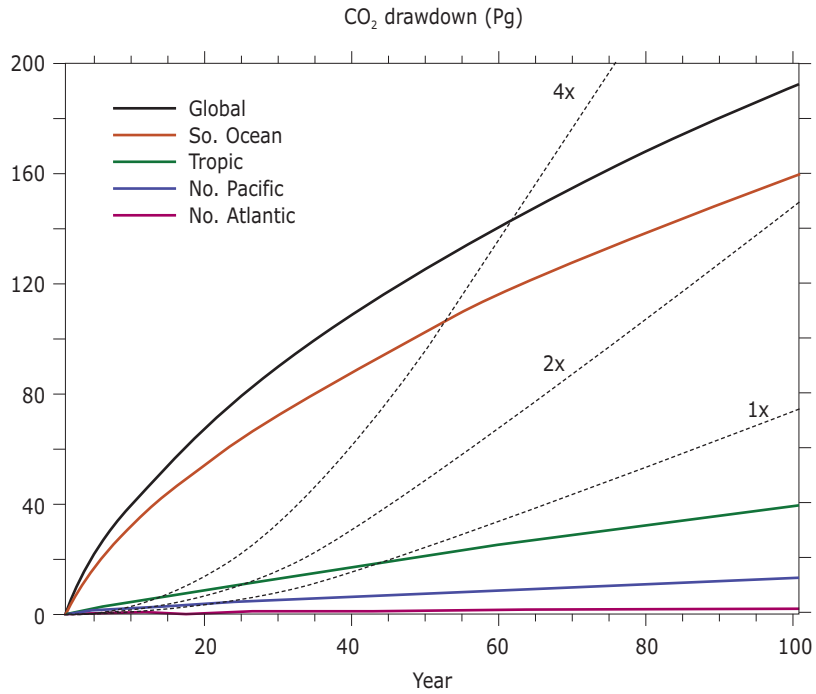
As already noted, simulations in which nutrients are drawn down at the surface in a diagnostic biology model (table 4.1a, page 76) show that a global drawdown of nutrients could remove 91 Pg C from the atmosphere (~43 ppm) over 50 years or 178 Pg C (83 ppm) over 2000 years. These simulations include the CO_2 lost from the ocean due to the declining concentration of CO_2 in the atmosphere. However, they do not include the effect on the ocean buffer capacity of increasing atmospheric CO_2 due to the anthropogenic sources. The atmospheric p_{CO_2} increase due to the anthropogenic sources reduces the buffer capacity of the ocean, $\partial DIC/\partial CO_2$, thereby resulting in increased oceanic CO_2 uptake following iron fertilization (cf., Cao and Caldeira 2010) relative to our simulations. The long term response of global iron fertilization is a potentially significant fraction of the 100 ppm

change needed to explain the glacial/interglacial atmosphere difference and would be even larger if the long term $CaCO_3$ feedback were included (e.g., Archer et al. 1998). What can we say about the short term response to surface nutrient drawdown? And given that iron fertilization has been proposed as a carbon mitigation strategy for these shorter time scales, what can we say about how much nutrient drawdown would result from iron addition?

We take as a metric for the iron fertilization impact the wedges concept introduced by Pacala and Socolow (2004). They proposed that humanity could act to stabilize atmospheric CO_2 at about 500 ± 50 ppm by avoiding an amount of projected future CO_2 emissions equivalent to 7 wedges, each of which consists of a total avoided emission of 25 Pg C increasing linearly from 0 Pg C yr^{-1} or avoided emissions in 2005 and ending at 1 Pg C yr^{-1} fifty years later. Each wedge represents a massive societal effort, for example the replacement of coal and gas power plants by tripling global installed nuclear capacity. The impact of such strategies is illustrated in figure 4.5, where the dashed black lines show the cumulative emissions reduction from implementing one, two and four wedges and the colored lines show fertilization in different regions from the fixed atmosphere model used to generate the results shown in table 4.1c (page 76). Over the first 50 years, ocean fertilization results in apparently significant emissions reductions, particularly if the Southern Ocean is fertilized. But because the impact of fertilization saturates, emissions avoidance strategies eventually win out. Note that this analysis assumes that iron fertilization is carried into the future indefinitely; if it is not, the sequestered carbon would start to leak back to the atmosphere. Ocean iron fertilization thus represents at best a strategy for delaying the necessary implementation of changes in energy use rather than providing permanent reductions.

We consider next how a more realistic representation of the impacts of higher iron delivery to the oceans affects the atmospheric CO_2 drawdown. One potential issue with the nutrient drawdown results reported in table 4.1a (page 76) is that biological cycling can only draw down carbon during the summer months, while deep water formation that injects carbon into the deep ocean occurs during the winter months. Marinov (2005) addressed this issue by performing nutrient depletion in different regions of the Southern Ocean during the Southern Hemisphere winter (June, July, August), the Southern Hemisphere summer (December, January, February), as well as during the entire year (table 4.2, page 78). Somewhat surprisingly, depleting

Figure 4.5: Response of atmospheric carbon inventory (Pg C) to suppression of emissions by 1, 2, and 4 wedges (dashed lines) versus nutrient depletion. The fixed atmosphere simulations are summarized in table 4.1c and indicated in the figure by the colored solid lines.



nutrients during the three summers accounted for 60% of the carbon uptake resulting from the equivalent yearlong depletions and had a similar impact as the (unrealistic) wintertime nutrient depletion experiments. In this model, summertime waters depleted in nutrients still provide a significant fraction of the waters ventilating the deep ocean. Depleting nutrients in the summer results in a smaller increase in Southern Ocean production and a smaller decrease in production north of 30°S compared to winter depletions. Thus, when measured relative to local changes in biological productivity, summer depletion is more effective in reducing atmospheric p_{CO_2} than winter depletion, i.e., it has a higher physical-chemical efficiency ($e_{phys\text{-}chem}$ of Equation (4.4), but defined relative to increased productivity south of 30°S rather than over the whole world table 4.2).

While nutrient depletion simulations provide an upper limit for how much carbon can be drawn out of the atmosphere by the biological pump, they do not directly simulate the impact of iron fertilization *per se*. Ocean biogeo-

chemistry models with an explicit iron cycle as well as an ecosystem component that can simulate a wide range of processes such as light limitation have been in existence for several years now (e.g., Moore et al. 2002b; Aumont et al. 2003; Dutkiewicz et al. 2005; Tagliabue and Arrigo 2006). The representation of iron limitation and impact of its removal on carbon cycling varies substantially amongst these models.

The simplest representation is that of Zahariev et al. (2008) in whose model plankton growth is the *minimum* of light limited growth, nitrogen limitation, and a temporally constant iron limitation factor (iron cycling is not prognostically handled in this model) that is very low in the Southern Ocean, high in the subtropical gyres and at intermediate levels in the Equatorial Pacific and North Pacific. Iron limitation thus acts only when there is sufficient light and macronutrient; otherwise it has no impact on phytoplankton growth. Iron "fertilization" then consists of removing this limitation term but leaving the light limitation unchanged. Zahariev et al. (2008) find a maximum uptake of 1 Pg Cyr^{-1} from this perturbation, with 26 Pg C taken up over 100 yr, approximately one-fourth that of the nutrient depletion results in table 4.1a. Over thousands of years, they do find an uptake of 77 Pg C, a value significantly smaller than that needed to explain glacial-interglacial CO_2 variations. As noted by Marinov et al. (2008b) and Gnanadesikan and Marinov (2008), the increased biological storage of carbon is not necessarily associated with increased biological productivity. Zahariev et al. (2008) see a ~30% decrease in global primary productivity and export under global iron fertilization as more productivity is concentrated in the Southern Ocean.

Other relatively simple, yet prognostic, treatments of iron fertilization are those of Parekh et al. (2006) and Dutkiewicz et al. (2006) who simulate an iron cycle in the ocean but have a very simple treatment of how it affects nutrient uptake. In this model, the rate at which nutrients are taken up is the *product* of three limitation terms, one due to iron, a second due to the macronutrient phosphate and a third due to light. In this model, adding iron to the ocean removes carbon primarily in the tropics where light is high. The Southern Ocean is relatively insensitive to the addition of iron and an approximately fivefold higher dust delivery rate typical of the Last Glacial Maximum produces an atmospheric carbon dioxide drawdown of only ~8 ppmv. Making the ocean more iron limited does have a big impact on atmospheric carbon dioxide, however, as iron limitation can then shut down

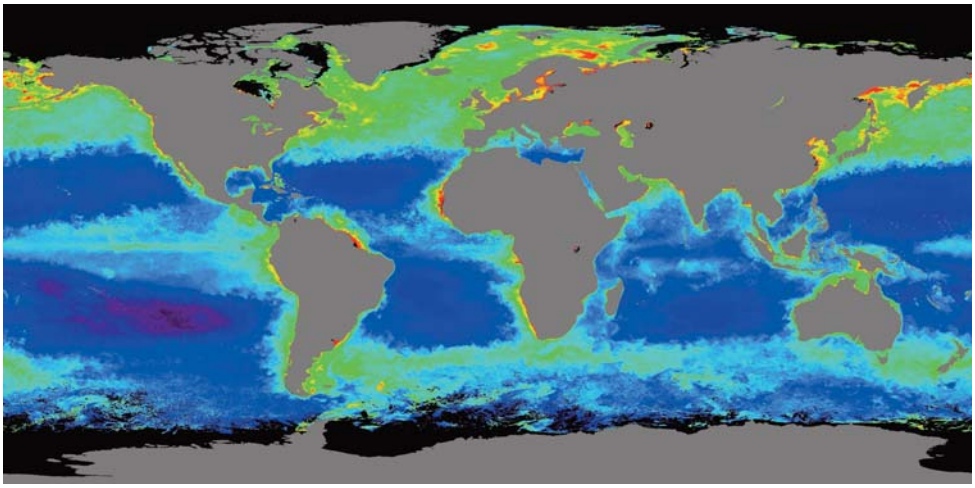
tropical production. Thus a fivefold decrease in iron delivery in this model results in an increase in atmospheric carbon of 181 ppm (map 4.3).

There are also a number of more comprehensive ocean biogeochemical models in which the iron cycle as well as its impact on phytoplankton physiology are directly represented (e.g., Moore et al. 2002b; Aumont et al. 2003; Dutkiewicz et al. 2005; Tagliabue and Arrigo 2006; Dunne et al. in prep.). In all of these codes, iron is allowed to affect the growth rates of individual groups of phytoplankton which then affect the cycles of phosphorus, nitrogen, oxygen and iron as the organic matter they produce is grazed and exported to depth. The representation of how iron limitation affects phytoplankton growth differs significantly across the models.

In Moore et al.'s (2002a) NCAR model and Aumont et al.'s (2003) PISCES model, iron limitation reduces the inherent growth rates of plankton through a Leibig-like "law of the minimum" in which iron only limits growth when it is the most limiting nutrient. Thus in regions where either phosphate or nitrate is limiting but iron is abundant, adding more iron will have little effect, though in the HNLC regions it will be important. Aumont and Bopp (2006) showed that their PISCES model was able to credibly simulate the increase in chlorophyll, diatom biomass and drawdown in surface p_{CO_2} found at a number of field studies. When large-scale iron fertilization was applied in this model, an atmospheric drawdown of 33 ppmv (70 Gt C) was found over a period of 100 years. In comparison to the model of Dutkiewicz et al. (2006), PISCES is much more sensitive to changes in iron supply in the Southern Ocean even though a large-scale fertilization does not deplete Southern Ocean nutrients completely.

In Dunne et al.'s TOPAZ model (in prep. and in appendix in Sarmiento et al. 2009), iron limitation also affects the growth rate of phytoplankton, but additionally reduces the ability of plankton to synthesize chlorophyll. This means that even in regions where iron is not the most limiting nutrient, adding iron can increase phytoplankton growth rates as it relieves light limitation. Thus while in the PISCES model adding iron makes plankton more light-limited, in the TOPAZ model increasing chlorophyll synthesis compensates this effect. Sarmiento et al. (2009) demonstrate that the TOPAZ model is also able to simulate the changes in chlorophyll found in a number of field experiments. Iron fertilization was simulated in this model by removing the effects of iron limitation from phytoplankton growth terms. The resulting drawdown from large-scale fertilization (shown in table 4.1b, page 76) is about 80% of the nu-

Map 4.3: Chlorophyll levels. Observation of global chlorophyll patterns shows where ocean surface plants phytoplankton are growing, and gives an indication of where marine ecosystems are thriving. Maps like this give an idea of how much carbon the plants are soaking up, which is important in understanding the global carbon budget.



trient depletion runs after 50 and 100 years, somewhat larger than Aumont and Bopp (2006), consistent with iron having a somewhat larger impact in high-latitude regions. Most of this difference is attributable to the Southern Ocean. As compared with the nutrient depletion simulations, the tropics show a higher impact from fertilization than do the nutrient depletion simulations, while the North Atlantic shows an order of magnitude lower impact.

In understanding the TOPAZ model results, a number of subtleties need to be taken into account. The first is that the response of the carbon cycle to changes in iron fertilization will depend on the initial state of the ocean biogeochemistry and carbon cycle model. The nutrient depletion results in table 4.1a have as a control a model in which surface nutrients are forced towards their observed concentrations. By contrast, the TOPAZ model used for the simulations shown in tables 4.1b and 4.1c predicts overly high nutrients in the tropics and overly low nutrients in the North Atlantic. As such, the predicted responses to nutrient removal in these two regions shown in tables 4.1b and 4.1c (page 76) are correspondingly distorted. Tables 4.1a and 4.1b would be very close to each other if the control simulations in the prognostic model were more realistic, but in fact the North Atlantic CO_2 response in table 4.1b is $1/10^{th}$ that in table 4.1a, and the tropical result is about twice as large. Since this is due to a poor baseline simulation in the TOPAZ model we discount these particular results.

The second subtlety is the impact of source and sink changes on the atmospheric CO_2 reservoir. Suppose that we remove a wedge of carbon from the atmosphere, i.e., 25 Pg C over a 50-year period. One might think that this would result in 25 Pg C less CO_2 in the atmosphere than otherwise would have been there at the end of the 50 year period (which, divided by the 2.13 Pg C per ppm conversion factor, is equivalent to 11.8 ppm). However, this assumption would be incorrect because the reduced growth rate of atmospheric CO_2 resulting from the CO_2 removed from the atmosphere would lead to less CO_2 uptake by the ocean (the land may do the same but is much more complicated and beyond the scope of this paper). As a result, the actual reduction in atmospheric CO_2 resulting from the removal of CO_2 into the ocean would be less than 25 Pg C (cf. Gnanadesikan et al. 2003; Oschlies 2009; Sarmiento et al. 2009).

The importance of the back flux of carbon to the atmosphere is illustrated in table 4.1. Tables 4.1a and 4.1b show how much CO_2 is removed from the atmosphere in an iron fertilization simulation with an interactive atmosphere, where a removal of CO_2 from the atmosphere leads to a reduction of atmospheric CO_2 and thus a degassing of CO_2 from the ocean. By contrast, table 4.1c shows what happens when this effect is ignored by keeping the atmospheric CO_2 fixed (which, by the way, does not conserve carbon). Comparison of tables 4.1b and 4.1c, which are runs done with the same ocean model, shows that after 50 years the simulation with an interactive atmosphere has only 55% to 60% of the CO_2 removal than the fixed atmosphere simulation does. Which number should we use to analyze the impact of iron fertilization? If we want to compare the iron fertilization with the wedges, which refer to a change in the source of CO_2 to the atmosphere, not to a change in atmospheric CO_2 content, we should use the fixed atmosphere results in table 4.1c; and if we want to know the reduction in the atmospheric CO_2 growth rate that would result from a given fertilization scenario, we should use the results in tables 4.1a and 4.1b.

Finally, we note the important role of oceanic circulation and mixing in determining how much carbon dioxide is removed from the atmosphere in a large scale fertilization simulation. In Marinov et al. (2008b) we proposed that modelers measure the sensitivity of atmospheric carbon dioxide to iron fertilization (or, more broadly, to any change in the biological pump) relative to the total remineralized carbon inventory of the ocean. Equations (4.1) and (4.2) imply that this sensitivity will decrease with the remineralized carbon inventory (OCS_{soft}) and PO_{4remin}, and it will increase with the preformed nutrient inventory:

$$Sensitivity = -\frac{\Delta p_{CO_{2a}}}{\Delta OCS_{soft}} \approx \frac{c}{a_1} \cdot e^{-\frac{OCS_{soft}}{a_1}} + \cdots \approx \frac{c}{a_1} \cdot e^{-\frac{r_{C:P} \cdot (\overline{PO_4} - \overline{PO_{4pref}}) V_{oc}}{a_1}} + \cdot \quad (4.5)$$

where Δ stands for the respective changes with fertilization. The sensitivity to prolonged (century to thousand year time scale) large scale nutrient depletion in a suite of ocean only General Circulation Models (GCMs) with different oceanic circulations is shown in figure 4.6. Models with high vertical diffusivity or high Southern Ocean winds have higher deep ocean ventilation as indicated by their $\Delta^{14}C$, resulting in more nutrients in the preformed form (see Section 4.1) and a lower remineralized carbon storage OCS_{soft}. Models with initially weak total carbon storage such as the high ventilation models have more room to increase their carbon storage and therefore respond more to decreases in surface nutrients. In fact, high ventilation models will be more sensitive to any kind of changes in the biological pump than lower ventilation models. Slow CO_2 exchange at the air-sea interface significantly enhances the sensitivity difference between low ventilation and high ventilation models (figure 4.6) and makes the high ventilation models significantly more efficient at drawing down atmospheric carbon. This theoretical analysis has implications for the future climate. If Southern Ocean circulation were to intensify with climate change following an increase or poleward shift in Southern Ocean westerlies, atmospheric p_{CO_2} might become ever more sensitive to changes in Southern Ocean surface nutrients such as those induced by iron fertilization.

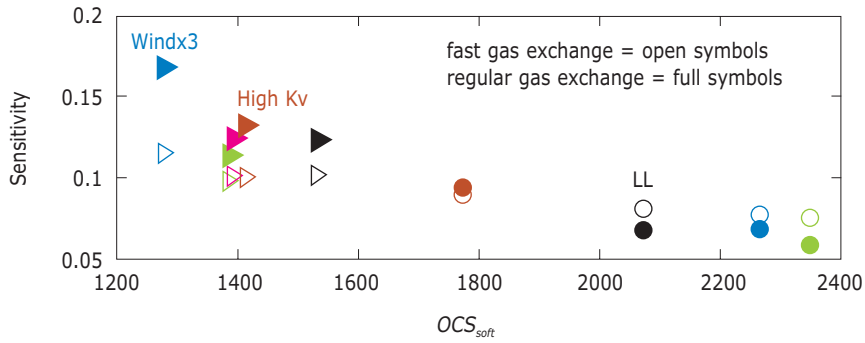
4.4. IMPLICATIONS FOR CARBON MITIGATION

Studies of the issue of iron fertilization for carbon mitigation have centered primarily on determining: 1) the *efficiency* of the fertilization; 2) the *verifiability* of CO_2 removal from the atmosphere; and 3) the long term *environmental consequences* of the fertilization (cf. Chisholm et al. 2001; and Buesseler et al. 2008). This paper has focused thus far on the underlying scientific issues regarding the connection of iron, the marine biosphere and the air-sea balance of carbon dioxide. In this section we present a brief discussion of the issues of verifiability and environmental consequences.

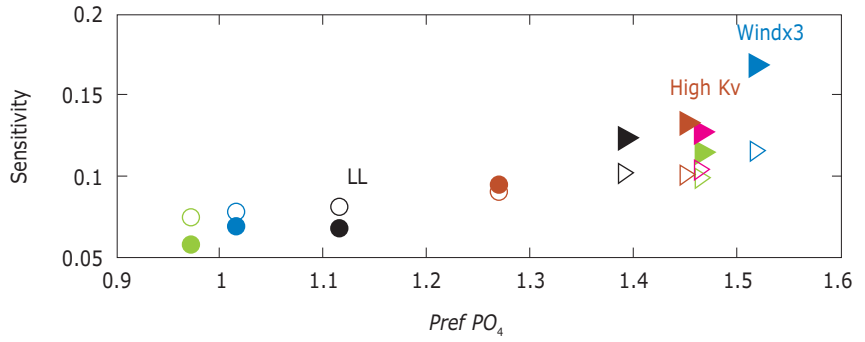
Verifiability of carbon uptake is a particularly difficult challenge for fertilization efforts. As has repeatedly been emphasized in this paper, marine biota modulates the air-sea balance of carbon by associating carbon with nutrients. But determining changes in the preformed and remineralized nutrient pools in the

Figure 4.6: Sensitivity of atmospheric p_{CO_2} to Southern Ocean nutrient depletion plotted against: a) Ocean carbon storage $OCS_{soft} = r_{C:P} \cdot (\overline{PO_4} - \overline{PO_{4pref}})$ before depletion (i.e., in the control simulation). **b)** Globally averaged preformed PO_4 before depletion. **c)** Globally averaged $\Delta^{14}C$ at 1500 m depth. Sensitivity defined as $-\Delta p_{CO_{2atm}}/\Delta OCS_{soft}$. Fast gas exchange (open symbols) and regular gas exchange (filled symbols) simulations shown for eight different ocean only GCMs. High ventilation models (triangles) have higher sensitivity than lower ventilation models (circles). Regular gas exchange enhances this effect. The vertical line in panel (c) shows the observed $\Delta^{14}C$ at 1500 m from GLODAP.

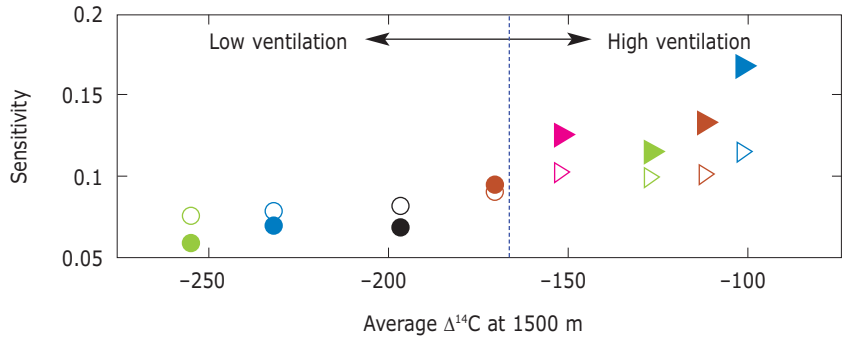
a)



b)



c)



Source: Marinov et al. 2008b.

ocean is not straightforward, particularly in the presence of changing circulation and global-warming dependent changes in oxygen. As seen by Marinov et al. (2008b), Zahariev et al. (2008), and Gnanadesikan and Marinov (2008), simply measuring the export of carbon to the abyss is insufficient-more storage of carbon dioxide in the ocean may be associated with less export. The problem becomes even more fraught for large scale patch fertilizations proposed by commercial ventures. As noted by Gnanadesikan et al. (2003), the changes in air-sea carbon flux associated with such activities have spatial scales of thousands of km and temporal scales of months. The fluxes associated with the net uptake represent a small fraction of the background carbon cycle. Additionally, both Gnanadesikan et al. (2003) and Sarmiento et al. (2009) show that the net uptake of carbon by the ocean from a transient iron fertilization depends sensitively on the cycling of iron and carbon within the water column. If iron is rapidly lost, the carbon initially taken up by iron fertilization outgases over long times and large spatial scales. Finally, as noted above, oxygen changes associated with fertilization can lead to denitrification- reducing remineralized nutrients leading to a carbon flux back to the atmosphere.

The potential environmental consequences of extensive iron fertilization alone are sufficient to give pause to anyone seriously considering this as an option for CO_2 removal, as discussed by Chisholm et al. (2001), Jin and Gruber (2003), Schiermeier (2003), Shepherd (2009), and Strong et al. (2009) among others. Potential side effects of ocean iron fertilization include: 1) changes in global patterns of nutrients and ocean productivity, 2) oxygen depletion and changes in the extent and frequency of hypoxia, 3) increased emissions of nitrous oxide and methane, both potent greenhouse gases, 4) alteration of ocean ecology and resulting changes in DMS. Below we briefly discuss each of these.

1) Iron fertilization will reduce the supply of nutrients to surface waters downstream of the fertilized region. Reduction in the macronutrients returning to the ocean surface decreases primary production on the multi-decadal to century timescale, as indicated by model projections of large-scale fertilization in Gnanadesikan et al. (2003), Aumont and Bopp (2006), and Zahariev et al. (2008). A particular striking result follows long-term iron fertilization of the Southern Ocean and is summarized in figure 4.4 from Marinov et al. (2006). Up to two thirds of the low latitude production is fueled by preformed nutrients from the Southern Ocean surface, carried here by the Mode and Intermediate Waters (Sarmiento et al. 2004). Southern Ocean fertilization north of

the biogeochemical divide (i.e., in the Subantarctic region) consumes these preformed nutrients locally and therefore decreases nutrient availability and export production in low latitudes. By contrast, nutrient fertilization performed south of the biogeochemical divide (i.e., in the Antarctic region close to the Antarctic continent) will have minimal impacts on productivity in the rest of the ocean. Because of its large impact on atmospheric CO_2 and relatively small impact on global biological productivity, the area south of the biogeochemical divide emerges as the best candidate for potential Fe fertilization experiments.

2) Iron fertilization will not only increase export production locally at the ocean surface but also increase remineralization and thus oxygen consumption in the ocean interior. Models predict that prolonged fertilization will result in reduced deep ocean oxygen concentrations (e.g., Sarmiento and Orr 1991).

3) Nitrification (the oxidation of ammonium to nitrate with N_2O as an intermediate product) is the main source of nitrous oxide (N_2O) in the open ocean. At low oxygen concentrations, the ecology shifts toward microbes that produce methane and nitrous oxide (N_2O) through nitrification. Most of this newly produced N_2O eventually reaches the surface and is vented to the atmosphere, where it is a much more powerful greenhouse gas than CO_2. Mesoscale iron addition experiments have shown negligible to minor increases in N_2O production, whereas models of long-term ocean iron fertilization suggest significant N_2O production (Law 2008). The degree to which the resulting N_2O emissions might offset the radiative benefit from the CO_2 reduction depends on the location and duration and areal extent of fertilization (Jin et al. 2008) as well as the rate of vertical particle export.

   Rapid sinking of particles would limit N_2O production in the upper water column and maximize the time period before it is vented to the atmosphere (Law 2008). Because of this, Jin and Gruber (2003) find the largest N_2O fluxes to the atmosphere when fertilization, particularly of limited duration and size, is undertaken in the tropics. Smaller but significant offsets are found with Southern Ocean fertilization.

4) Iron fertilization alters the species composition of phytoplankton. An initial increase in small phytoplankton abundance is followed by a shift to increased diatom biomass (Marchetti et al. 2006), with consequences for

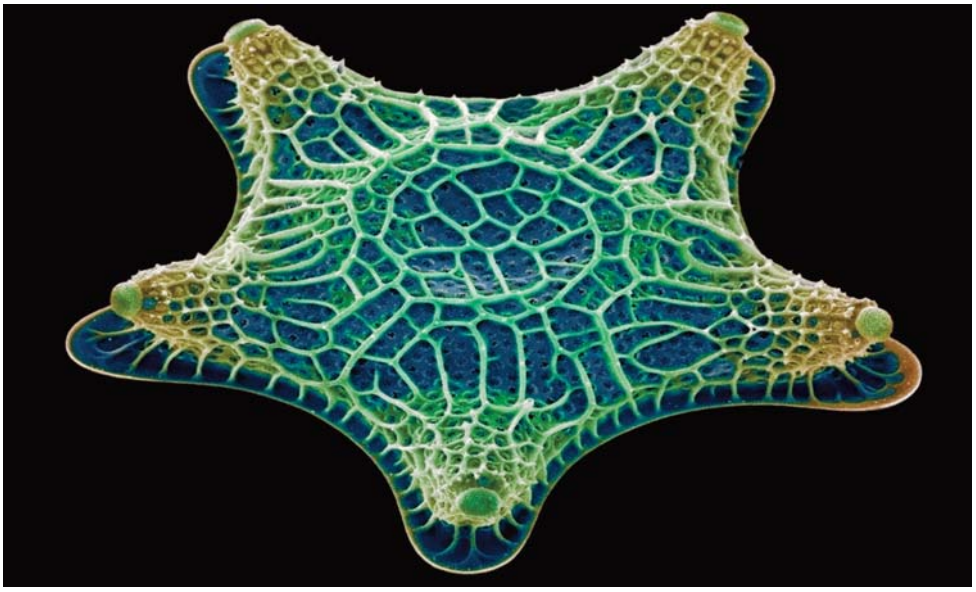


Photo 4.3: Diatom, a planktonic marine unicellular alga. Colored scanning electron micrograph (SEM) of a *Triceratium* sp. diatom.

zooplankton distribution and greater drawdown of silicic acid relative to nitrate (Boyd et al. 2004) (photo 4.3). Iron fertilization experiments can also stimulate small phytoplankton producing dimethylsulfide (DMS), the largest natural source to the atmospheric sulfur budget and a stimulus for the formation of cloud condensation nuclei. Increased input of sulfur to the atmosphere could potentially increase the earth's albedo, enhancing the climate-mitigation effects of iron fertilization. However, mesoscale experiments suggest a complex story, with the resulting DMS signal dependent on the location of the fertilized area (Law 2008). In mesoscale experiments, iron depleted Southern Ocean waters represented a significant DMS source to the atmosphere (Boyd 2007) while iron depleted Subarctic Pacific waters were either a sink or showed no significant change in DMS (Levasseur et al. 2006).

4.5. CONCLUSIONS

We have seen that the marine biosphere exerts an important control on the air-sea balance of carbon dioxide via the biological carbon pump. This balance is particularly sensitive to both physical and biological changes in the

regions that ventilate the ocean's deepest waters, particularly the Southern Ocean south of the polar front. These regions are particularly important because nutrients are not used up in surface waters, thus allowing carbon taken up with nutrients elsewhere in the ocean to escape to the atmosphere and injecting preformed nutrients into the deep ocean.

On glacial-interglacial time scales, changes in the ocean biological carbon pump remain a possibility for explaining changes in atmospheric carbon dioxide. The extent to which such changes are driven by changes in upwelling, changes in iron fertilization, or both remains unclear. As we have shown here, some realistic models of ocean biogeochemistry, including the carbon cycle, show that relieving iron limitation in the Southern Ocean is capable of removing significant amounts of carbon dioxide from the surface ocean over centennial time scales, while others do not. This uncertainty highlights the importance of better characterizing the ocean iron cycle as well as understanding how iron affects plankton in realistic environments.

As we have discussed, however, iron is not the only means by which the biological carbon pump may change. A recent paper by Anderson et al. (2009) notes that increases in atmospheric carbon dioxide during the last deglaciation coincide with increases in opal burial in the deep ocean. This correlation is used to argue that a change in the ventilation of the deep ocean drives the repartitioning of carbon dioxide, rather than changes in iron supply. It should be noted that changes in circulation and iron fertilization should not be considered in isolation. Parekh et al. (2005) found that a reduction in the upwelling of deep, iron poor water in the Southern Ocean could enhance the sensitivity of the ocean to iron fertilization by making it easier to draw down surface nutrients. Their work highlights the importance of understanding nutrient and carbon cycling in the regions that ventilate the deep ocean as well as how the fluxes of such source waters may have changed over time.

Finally, we have examined potential impacts of attempts to manipulate marine biota so as to mitigate emissions of greenhouse gases by accelerating the uptake of carbon by the ocean. While our studies indicate that significant amounts of carbon could be sequestered through such methods, this can only be done by fertilizing vast regions of the Southern Ocean. We note that such large-scale sequestration would involve massive changes in oceanic ecosystems, particularly in the Southern Ocean, that verifying the resulting uptake of carbon would be difficult, and that there are significant possibilities for negative consequences.

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