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Marine biological controls on climate via the carbon and sulphur geochemical cycles

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We review aspects of the influence of the marine biota on climate, focusing particularly on their role in mediating surface temperatures via their influence on atmospheric carbon dioxide (CO_2) and dimethyl sulphide (DMS) concentrations. Variation in natural CO_2 concentrations occurring over 10^3–10^5 years are set by oceanic processes, and in particular by conditions in the Southern Ocean, so it is to this region that we must look to understand the glacial–interglacial changes in CO_2 concentrations. It seems likely that marine productivity in the Southern Ocean is limited by a combination of restricted iron supply to the region and insufficient light.

Plankton-produced DMS is thought to influence climate by changing the numbers of cloud condensation nuclei available in remote regions; the efficiency of this mechanism is still unknown, but calculations suggest it may be a powerful influence on climate. It has a much shorter time-scale than the CO_2 effect, and as a consequence may well be a player on the 'global change' time-scale. The direction of both the CO_2 and the DMS mechanisms is such that more marine productivity would lead to lower global temperatures, and we speculate that the overall effect of the marine biota today is to cool the planet by *ca.* 6 °C as a result of these two mechanisms, with one-third of this figure being due to CO_2 effects and two-thirds due to DMS.

While the marine biota influence climate, climate also influences the marine biota, chiefly via changing atmospheric circulation. This in turn alters ocean circulation patterns, responsible for mixing up sub-surface nutrients, and also influences the transport of nutrients, such as iron, in atmospheric dust. A more vigorous atmospheric circulation would be expected to increase the productivity of the marine biota on both counts. Thus during glacial time, the colder and drier climate might be expected to stimulate greater marine productivity than occurs today. Since more production leads to greater cooling by reduction in CO_2 and increase in DMS, the marine biota–climate system appears to have been in positive feedback in the glacial–interglacial transition, with the changes in the climate system being reinforced by changes in the marine biota. In the context of anthropogenic change, we cannot at present say what sign the feedback on climate will have, because we have no clear idea whether circulation will become more or less vigorous in the future.

Keywords: carbon dioxide, dimethyl sulphide, phytoplankton, climate change, palaeoclimate

1. INTRODUCTION

The phytoplankton of the world's oceans are mostly unicellular organisms, no bigger than a few tens of microns in size. They live only a matter of days and seem individually insignificant. Even their total mass is very small compared to the mass of vegetation on the land surfaces. But globally, the productivity of the plankton is comparable to that of the land vegetation (Longhurst *et al.* 1995), and collectively their effects on the climate, chemistry and geology of the planet have been, and continue to be, profound.

The marine biota affect and interact with the climate on many different time-scales. These range from the seasonal (e.g. the annual 'blooming' of the North Atlantic or the response to the monsoons in the Indian Ocean), up to the periods of more than 10^7 years over which carbon is removed from the atmosphere–ocean system to form carbonate rock and organic deposits—part of the rock cycle which over long timespans is thought to control atmospheric carbon dioxide (CO_2) concentrations (Berner *et al.* 1983). For a short article such as this, we have chosen to limit our discussion to the marine biota's influence on climate via modulation of atmospheric CO_2 and sulphur gas concentrations over times of 1–10^5 years—of particular relevance to the Pleistocene glaciations. After describing the basic mechanics of these two kinds of marine biota–climate interactions, we then evaluate the probable magnitude of the effects over the last glacial cycle, and demonstrate that the marine biota–climate system appears to have been in positive feedback with respect to these changes.

2. MARINE BIOLOGICAL CONTROLS ON ATMOSPHERIC CO_2

(a) *The marine biota's effect on atmospheric CO_2*

Figure 1 is a reservoir-flux representation of the steady-state, pre-industrial global carbon cycle. It is adapted from several sources (Houghton *et al.* 1990; Sarmiento &

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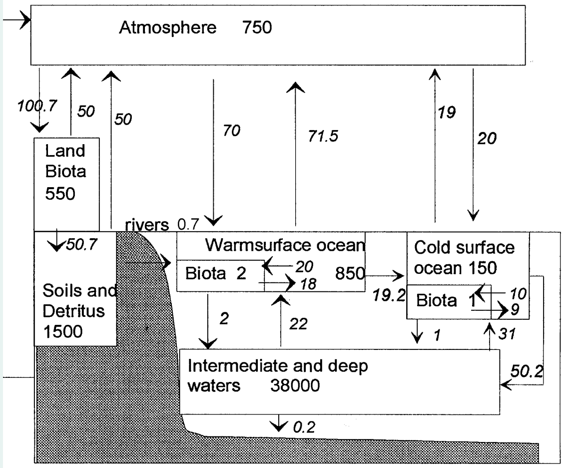


re 1. Reservoir-flux representation of the steady state, ndustrial global carbon cycle. Reservoir sizes are in Gt of ıd fluxes in Gt C yr^{-1}. The figure is adapted from ghton *et al.* (1990), with additional information from iento & Sundquist (1992), Sarmiento & Toggweiler 4), and Sundquist (1985). Fluxes are adjusted so that the ux into each reservoir is zero, which sometimes involves fying fluxes to a higher accuracy than that to which they ı reality known.

lquist 1992; Sarmiento & Toggweiler 1984). The numer- values assigned to the fluxes have been adjusted so that luxes into and out of each reservoir are zero, and also so there is approximately the correct net flux around in loops; for example, the ocean–atmosphere–land– circuit is approximately 0.5 GtC yr^{-1} (Sarmiento & lquist 1992) while the volcanic efflux–land–river–sedi- flux is 0.2 Gt C yr^{-1} (Sundquist 1985), and the warm n–atmosphere–cold ocean circuit is about 1 Gt yr^{-1}. To eve this self-consistency it is necessary to specify some s to three significant figures, but this should not of se be taken to imply that we know the true values to t accuracy.

ıe figure serves to focus attention on the reasons why narine biota are implicated in changes in atmospheric . Nine-tenths of the carbon in the system is in the deep This reservoir is continually being mixed and brought cean surfaces by fluxes of upwelling water which, in ıbsence of the marine biota, would bring the concen- on of carbon at the surface up toward that in the deep within a matter of only a few decades. The ocean ce forms the only route for communication between large deep-sea reservoir and the remainder of the m.

xamining this remainder, that is the atmosphere, n surface and terrestrial components of the carbon , we see that the fluxes between these components arge compared to the amounts of carbon in the reser- , such that the time-scale for approaching steady state ng these components is short. The largest time-scale is t 100 years for turnover of soils and detritus. Over er periods of time, therefore, the system is governed he conditions set up in the ocean surface. In parti- , since atmospheric CO_2 must be close to librium with surface water CO_2, the concentration of in the atmosphere will tend to adjust itself to a value y conditions in the ocean surface.

Imagine, for example, that some change in climatic conditions causes an increased flux of carbon from the terrestrial biosphere. Increasing the flux from the land biota to the atmosphere by 10% would cause atmospheric CO_2 to rise dramatically, at a rate of *ca.* 0.5% per year, but it could not be sustained for longer than about 200 years because all of the carbon in the land biota and soils reservoirs would be used up in that time. Over these time-scales the land biosphere and the atmosphere *must* be in steady state, and the atmospheric CO_2 concentration must therefore be set by conditions in the surface ocean, which 'regulates' contact between the atmosphere and the deep-sea reservoir.

The marine biota work continually to reduce the amount carbon in surface water, by taking up dissolved carbon into their bodies. When these organisms die or are eaten, the carbon becomes part of a sinking rain of detritus which falls out of the surface ocean under the influence of gravity. Their effect on the concentration of carbon in surface water is quite modest; as the diagram shows, they serve to remove only about 10% of the upwelling carbon. However, atmospheric CO_2 is sensitive to the partial pressure of CO_2 (pCO_2) in equilibrium with seawater, and not the total content of inorganic carbon, and the impact on pCO_2 is considerably greater than might be expected because of the amplifying effect of the chemistry of CO_2 in seawater. This is quantified in the Revelle buffer factor (β), which has a value ranging from about 8–15 in surface water. β is defined as the fractional change in pCO_2 which accompanies unit fractional change in total inorganic carbon concentration when other factors are constant. If $\beta=10$, therefore, a 1% change in total carbon causes a 10% change in pCO_2. The buffer factor is itself a function of total carbon content, so in detail the calculation is nonlinear and slightly more complex. Results of a full calculation are shown in figure 2, where a 'Strangelove ocean' is modelled using the formulation of Sarmiento & Toggweiler (1984). In this scenario, all marine life is assumed to die at time $t=100$ years. The concentration of CO_2 in the atmosphere rises by a factor of nearly 2, with a $1/e$ time of *ca.* 100 years.

(b) *Limits to the marine biota's effect on atmospheric CO_2*

In textbooks written up to the mid-1980s (i.e. Broecker & Peng 1982) it is stated that marine biota are limited by the amount of the macronutrients phosphate and nitrate in deep water. For reasons which are still not fully understood, nitrate and phosphate are present in deep water in a ratio which is very close to that in which the biota require them. It matters little therefore whether we state the limitation in terms of phosphate or nitrate.

(A cautionary word about semantics may be appropriate here. Chemical oceanographers often talk of 'limitation' of the 'productivity' of the marine biota, just as we do in this paper. In almost all cases, they do not mean the same as would a biologist using the same words. A biologist would probably point out that a marine ecosystem is most unlikely to be limited by one or two inorganic nutrients only. An ecosystem consists of many species, each of which is limited by a different set of factors. However, if we are interested in what sets atmospheric CO_2, it is only the concentrations of

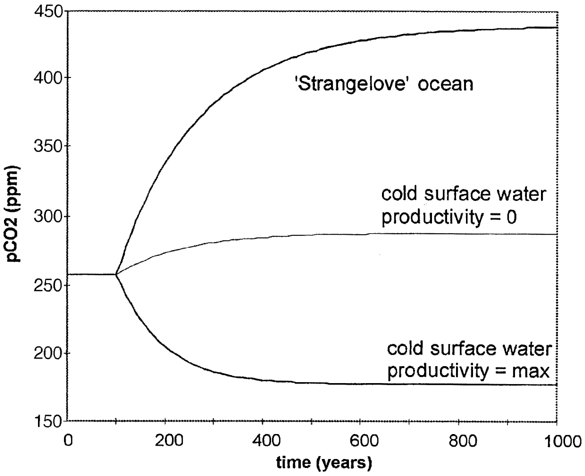


Figure 2. Effects of marine biota on atmospheric CO_2 from a simple model. In each run, the model of is initialized at (pre-industrial) steady state. At $t=100$ years, a perturbation is applied. For the 'Strangelove ocean', all marine biological activity is stopped instantaneously. 'Cold water productivity = 0' and 'cold water productivity = max.' show the possible extremes to which atmospheric CO_2 can be driven by modulating the efficiency of the cold-water marine biota. The model of Sarmiento & Toggweiler (1984) was used.

inorganic carbon chemical species at the ocean surface that are important. The chemist is therefore interested only in the factors that control the fraction of inorganic carbon converted to organic forms by the overall ecosystem. This is related to 'net ecosystem productivity' in the sense that an increase in this quantity would result in an increase in the efficiency of conversion if other factors remain constant. However, in general it is not identical to any biological measure of production, and is a measure of the efficiency of carbon uptake rather than of production in the strict biological sense.)

Support for the idea that phosphate and/or nitrate are the factors that limit the uptake of carbon can be found over large areas of the world's oceans. In the warm-water oceans, concentrations of these nutrients are frequently reduced to essentially zero at the surface. This suggested to earlier workers that the CO_2 concentration of surface waters (and hence the atmosphere) was largely constrained by the concentration of these nutrients in the deep sea (Broecker & Peng 1982). For example, according to the GEOSECS data (Takahashi *et al.* 1981), the deep North Atlantic contains typically 1.5 μmol kg^{-1} of phosphate, while the surface of the North Atlantic contains almost none. Phytoplankton can fix into their bodies about 140 atoms of carbon for each molecule of phosphorus they use. (The 'classic' ratio calculated by Redfield (1963) is 106, but this figure has been revised upwards in recent years: for examples, see Watson & Whitfield 1985; Takahashi *et al.* 1985). Thus, if deep North Atlantic water upwells to the surface, the biota might be expected to remove *ca.* 1.5×140 (= 210) μmol kg^{-1} of carbon as photosynthate. An additional 20% might be expected to be removed by incorporation of calcium carbonate into the tests of organisms. In fact, total inorganic carbon concentrations are typically 230 μmol kg^{-1} more in the deep Atlantic than in the surface Atlantic, so here at least this simple idea seems to work moderately well.

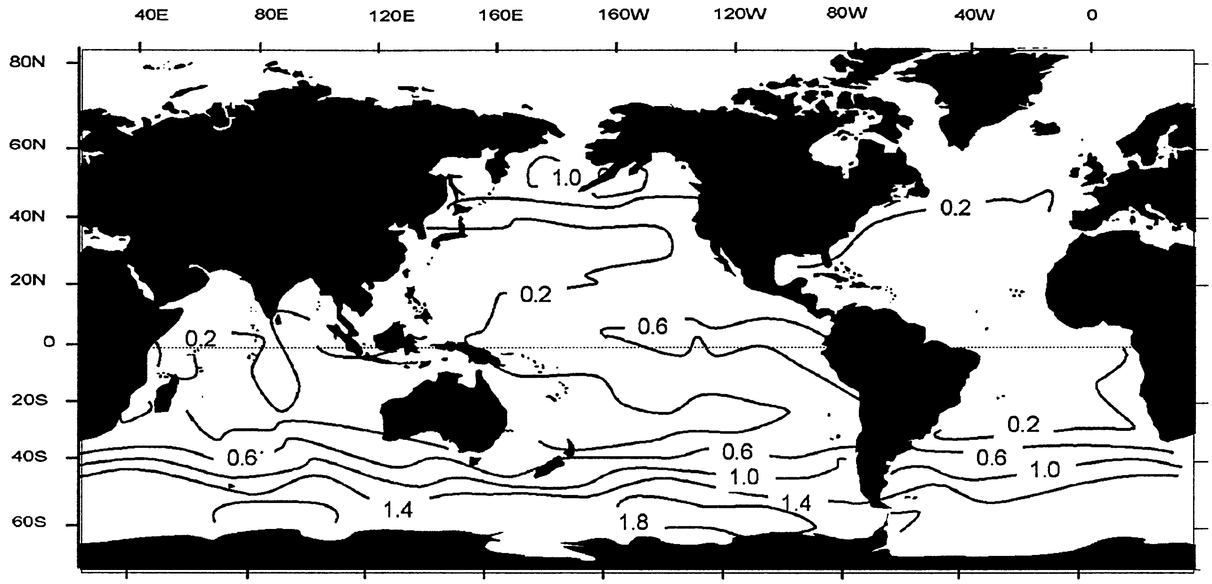
However, in practice, over substantial regions, this analysis does not hold. Figure 3, drawn from the data of Levitus *et al.* (1994), shows that in the annual average there is measurable phosphate at the surface of many of the world's oceans, and substantial quantities in three zones; the subarctic Pacific, the equatorial Pacific and the Southern Ocean. In modern parlance these regions are termed 'high nutrient, low chlorophyll' (HNLC) zones.

(c) *The importance of the Southern Ocean*

The most prominent HNLC region is the Southern Ocean, where typical ocean surface values of phosphate and nitrate are around two-thirds those of the deep water. Obviously, something other than the availability of these nutrients is limiting the uptake of inorganic CO_2. The Southern Ocean constitutes only 15% of the total of the world's oceans, which is the reason that it was ignored in earlier interpretations. However, more recent work has shown (Sarmiento & Toggweiler 1984; Siegenthaler & Wenk 1984; Knox & McElroy 1984) that this and other cold-water parts of the ocean's surface have an influence on atmospheric CO_2 out of proportion to their area. This reasoning suggests that the cold-water surfaces of oceans are particularly important in setting atmospheric CO_2 on time-scales of a few hundred years.

The reason for the importance of the cold-water oceans can be appreciated by referring again to figure 1. Water transfers from the deep sea to the ocean surface by upwelling both to the warm- and cold-water surface regions. (The warm-water surface can be thought of as all of the surface-mixed layer between about 50° N and 50° S, including the subtropical gyres and the equatorial upwelling systems.) However, especially given the smaller extent of the cold-water regions, upwelling of deep water into this reservoir is more intense than it is to the warm-water surfaces. Furthermore, transport *into* the deep ocean occurs almost exclusively from the temperate and cold-water surface zones. The great majority of the carbon flux into the deep sea is as dissolved CO_2 originating from these cold-water regions, so any process that influences the carbon chemistry of the water here will have a large effect on the amount of carbon entering the deep sea, and ultimately therefore on the steady state that results.

Now, referring to figure 1, consider what processes might cause concentrations of carbon in the surface waters to change. If we assume that concentrations of nutrient in the warm-water ocean surface are reduced to zero by the biota there, CO_2 concentrations are constrained within narrow limits. Assuming 'Redfieldian' stoichiometry, when the nutrient has been exhausted an equivalent amount of carbon will also have been removed. In the Southern Ocean cold-water regime, however, classical nutrient limitation does not apply and we must seek some other cause for the limitation of biological activity. Furthermore, because transport between cold surface water and deep water is much more rapid, changes in this region have a larger effect than would be guessed from their restricted area. In figure 2, we have shown the effect on atmospheric CO_2 of reducing the particulate flux in the 'cold water' ocean to zero, or of increasing it to the maximum extent possible (i.e. using up all the phosphate



'e 3. Global annual average surface phosphate concentrations (μmol kg^{-1}). 'HNLC' areas show up in the equatorial and h-East Pacific and Southern Oceans. Drawn from data in Levitus *et al.* (1994).

nitrate in the surface water). The model predicts that iderable modulation of atmospheric CO$_2$ about the ly state value will result, again on a time-scale of one vo centuries.

ie Southern Ocean, as the major region of intermediate deep water formation which is also a HNLC area, efore becomes critical in understanding what controls ospheric CO$_2$. This follows from the assertion that r enters the deep sea exclusively from the temperate/-water ocean surface, which is now in little doubt. In it years it has been possible to study this ventilation of leep sea by following the production of anthropogenic itants such as bomb-produced tritium and radiocarbon gweiler 1994; Broecker *et al.* 1985) and chlorofluoro-ons and related compounds (Gammon *et al.* 1982). Such es have shown with great clarity that the processes of mediate and deep water formation occur overwhel-gly at specific sites in temperate and polar regions, as the northern North Atlantic, the subantarctic ergence, and the Greenland, Labrador and Weddell . Except in the Mediterranean and other warm-water ginal seas, deep water simply does not form from n surface waters; if it did, the deep sea would be n, instead of being close to freezing. Furthermore, t measurements of vertical eddy diffusion across the nocline in the warm-water ocean have shown that sport across this barrier is very slow (Ledwell *et al.*). Warm surface water is too buoyant to mix into the sea; it has to be transported towards the poles, and in oing lose its heat to the atmosphere, before it can me sufficiently dense to be able to mix into the deep n.

ron and light

hat then sets the marine biological net production in cold-water ocean surface? It now seems most likely the efficiency of carbon and nutrient uptake in these ons is determined partly by the availability of iron to oplankton, and partly by lack of light.

Iron limitation has long been a candidate for explaining the existence of HNLC regions (Hart 1934). Circumstantial evidence supporting the case for iron has come from (i) the observation of very low concentrations of iron in surface waters (Martin *et al.* 1990), (ii) the fact that in restricted areas of high productivity iron concentrations have been observed to be elevated (Debaar *et al.* 1995), and (iii) *in vitro* fertilization experiments in which incubations of plankton collected in the region frequently have shown more rapid production if enriched with iron than do controls (Martin & Fitzwater 1988). This circumstantial evidence has not proved sufficient to convince sceptics of the dominance of a simple inorganic cause for the existence of HNLC zones (Frost & Franzen 1992).

Recent advances in technology now enable patches of water 10 km in size to be tracked over periods of one or two weeks (Watson *et al.* 1991*a*,*b*) and this has enabled enrichment experiments to be carried out in the open ocean. Two such iron-enrichment experiments (Ironex I and II) have now been carried out in the equatorial Pacific, the second largest HNLC region after the Southern Ocean. These, and particularly Ironex II, have shown in dramatic fashion that iron is limiting there; addition of nanomolar concentrations of iron to a patch of water about 10 × 10 km caused a massive diatom bloom (Coale *et al.* 1996), one effect of which was to reduce ocean surface pCO$_2$ by 80 μatm. (Cooper *et al.* 1996).

Iron is in short supply in the oceans because of the very low solubility of the Fe(III) form, which is the normal state of the Fe ion in oxygenated seawater. Measurements of iron in the Southern Ocean have established that the concentrations in surface waters typically are less than 0.1 nmol kg^{-1}, just as low as the concentrations found in the equatorial Pacific. At these levels, iron may be expected to be limiting to many species of phytoplankton, particularly diatoms that are the prime 'bloom-forming' organisms and which are normally responsible for a large fraction of the export of organic matter out of the surface layer. It is tempting, therefore, to extrapolate the Ironex results from the equatorial

Pacific to the Southern Ocean. However, in all respects other than the low iron concentrations, conditions in the Southern Ocean are almost as different as can be from those in the equatorial Pacific. In particular, light limitation is almost certain to play a role; for half the year the days are short and there is comparatively little light, while all through the year the high circumpolar winds cause the mixed surface layer to be considerably deeper than that of the equatorial Pacific, meaning that phytoplankton spend more of their time at depths away from the light.

Is there a way to tell to what extent it is iron, and to what extent light, that limits the Southern Ocean? The clearest answer will probably come from Ironex-type experiments in the Southern Ocean, and these will almost certainly be done in due course. For practical reasons it is more difficult to stage such experiments in the inclement environment of the Southern Ocean than the pleasant waters of the equatorial Pacific, but the necessary technical expertise now exists to enable them to be done.

Some clues can be gained from remote-sensing of the distribution of ocean productivity. On the now-famous NOAA-7 images of ocean colour, processed by NASA to yield chlorophyll concentrations, the Southern Ocean appears to be intermediate in productivity between the ocean deserts such as the subtropical gyres, and the highly productive North Atlantic and coastal zones. But regions in plumes downstream of the influence of land, such as the South Atlantic to the east of the Antarctic peninsula, the islands of the South Scotia arc, and Kerguelen, show up as having high productivity. It is hard to escape the conclusion that areas near land or shallow seas are somehow induced to be more productive, an observation which is equally true in the equatorial Pacific where the Galapagos Islands show a distinct plume. Such an observation argues an important role for iron, which would be sourced from the shallow-water sediments of these regions and the dust blown off ice-free land.

(e) *Response to the Mount Pinatubo eruption*

Another possible test for the hypothesis of Southern Ocean iron limitation comes from an examination of the response of the global ocean to the eruption of Mount Pinatubo in 1991. The eruption released 3–5 km^3 of crustal material into the atmosphere, about 3% of which by weight would have been iron. Most of this would have come down to earth rather rapidly, but a small proportion could have been injected into the stratosphere either as very finely divided particles or as volatile compounds. Subsequently, the stratospheric aerosol settled out over a period of about two years. This aerosol was observed to arrive over the Southern Ocean by about November 1991 (Saxena *et al.* 1995). Calculation (Watson 1997) suggests that if iron is limiting over much of the Southern Ocean, the rain of particulate iron might have been sufficient to raise net export production in that region by as much as 10^{14} mol of C over the ensuing austral summer.

Is there any way to know whether this actually happened? Possibly, because from the beginning of 1990, ultra-high accuracy measurements of atmospheric oxygen were being made by R. F. Keeling in both the Northern and Southern Hemispheres (Keeling & Shertz 1992). A combination of O_2 and CO_2 measurements offers a way to monitor the globally integrated activities of the biota, and to separate marine from terrestrial components, as has been shown by Keeling *et al.* (1996). Changes in net productivity in the oceans show up very quickly as parts-per-million changes in atmospheric O_2, but the corresponding change in CO_2 occurs more slowly and is damped by the large reservoir of carbon in the sea. In contrast, variations in production on the land surfaces should show simultaneous effects on atmospheric CO_2 and O_2.

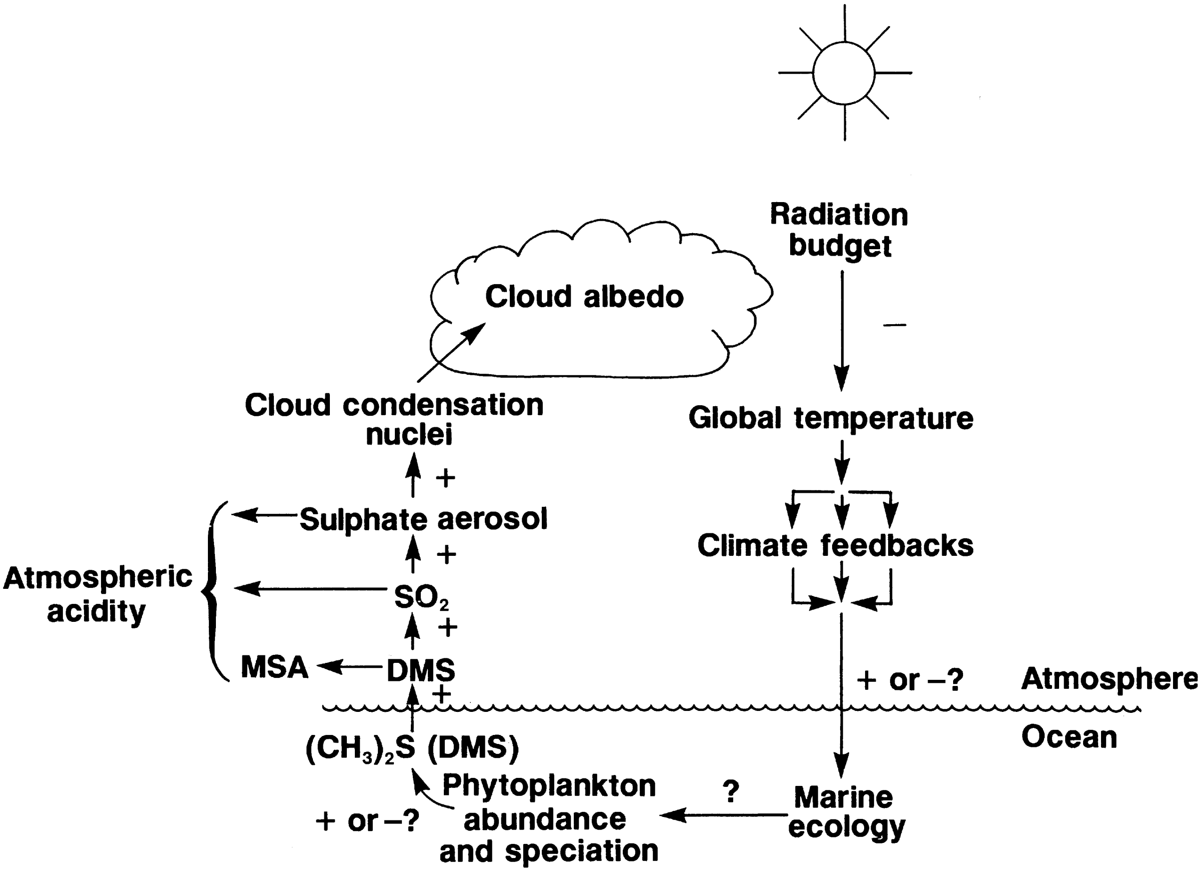
Keeling *et al.* (1996) remark that, in the austral summer following the Pinatubo eruption, their measurements are consistent with an anomalous 'pulse' of 10^{14} mol of O_2 being emitted from the Southern Hemisphere oceans. This is a substantial disturbance of the global marine carbon cycle (it corresponds to about one gigaton of extra carbon being transported out of the surface layer, a non-trivial fraction of the total export production by the marine biota in a year, according to figure 1). What we know of the response to the ocean following the Mount Pinatubo eruption does therefore support the idea that the Southern Ocean is substantially iron-limited, in summer at least.

3. MARINE BIOLOGICAL INFLUENCE ON CLIMATE BY PRODUCTION OF DIMETHYL SULPHIDE

Dimethyl sulphide (DMS) is produced by marine algae from the precursor compound dimethyl sulphoniopropionate (DMSP), which is metabolized by many species, but in different amounts. It is primarily known for its role as an intracellular osmoregulant. Since the surfaces of the oceans are always found to be supersaturated with DMS relative to its atmospheric concentration, there is a perennial net flux of the gas from the sea to the air. The magnitude of the flux is given by the product of the surface water concentration of DMS and a kinetic parameter (the transfer velocity), which quantifies the rate at which the gas crosses the air–sea interface and varies with factors such as wind, waves, bubbles and surface films.

Once in the atmosphere, DMS is subject to oxidation by free radicals, such as OH and NO_3, to form a variety of products including methane sulphonic acid (MSA) and sulphur dioxide (SO_2), which itself is oxidized, mainly in water droplets, to form sulphate. The cycle of production of DMS in seawater and its oxidation in the atmosphere is illustrated in figure 4. It is clear that the major oxidation products are acidic, and in the pristine marine atmosphere it is by this route that atmospheric aerosols and rain obtain most of their acidity. At the present time, the formation of SO_2 by man's burning of fossil fuel has considerably enhanced this acidity over major parts of the Northern Hemisphere, although for much of the Southern Hemisphere DMS oxidation is still the major source (Bates *et al.* 1992).

The climate role for DMS comes from the sub-micron sulphate particles resulting from its atmospheric oxidation (figure 4). These particles can interact both directly with sunlight (Shaw 1987) and indirectly by acting as the nuclei on which cloud droplets form (termed cloud condensation nuclei, CCN). The number and density of CCN are major determinants in cloud formation and thus



e 4. The mechanism suggested by Charlson *et al.* (1987) (see also Andreae 1990) by which marine dimethyl sulphide (DMS) ions from plankton influence climate via cloud properties. DMS is oxidized in the atmosphere to form acidic aerosols, which the major source of cloud condensation nuclei (CCN) in remote areas. Higher amounts of CCN lead to more reflective clouds, hereby a decrease in the absorption of solar radiation, lower surface temperatures and possibly other climatic effects too. This in turn have an influence on the rate of DMS emission, but the sign of this effect is unknown at present.

ie albedo of the planet (Charlson *et al.* 1987). Over , there is generally an abundance of CCN resulting soil dust blown into the air and from pollution es. However, over the oceans, far from land (i.e. the rity of the globe), the main source of CCN appears to rom the oxidation of DMS. This is supported by ous lines of evidence, including the chemical composi- of the CCN being largely sulphate (neutralized to extent by ammonia), and the coherence in the nality of both CCN number, density and cloudiness neasured by cloud optical depth), which in turn corre-d to the times when marine algae are actively ucing DMS in seawater (Boers *et al.* 1994; Liss & oway 1993). In their seminal paper Charlson *et al.* 7), having developed the idea of the link between S and cloud albedo, went on to speculate that the m might display negative feedback such that a ge in climate might be counteracted by a corre-ding but inverse change in the DMS–CCN–albedo , as indicated in figure 4. We return to this tantalizing bility later.

vomey (1991) has attempted to quantify the magni- of the effect of CCN (and hence droplet number) on do (reflectance), as illustrated in figure 5. We use this ram shortly to try to quantify the role of DMS uced by marine algae in cooling the planet. For the nent it is worth noting an important property of the CCN–albedo linkage. The diagram shows that the effect of CCN number on the incremental increase in albedo for each particle added (the susceptibility in figure 5) is much more pronounced at low particle numbers. Once the air contains several hundred particles or droplets per cubic centimetre, addition of further particles has little effect on cloud reflectance. Over and close to land CCN numbers generally exceed this level. Thus, we must look to oceanic areas, and particularly the Southern Hemisphere, with its much greater ratio of sea to non-ice-covered land area, for the greatest potential climatic impact of changing CCN numbers, whether the particles arise, for example, from alteration in oceanic DMS fluxes or from inputs of SO_2 from (increased) fossil fuel burning. To graphically illustrate the point, Twomey cites a calculation which shows that equal quantities of sulphur entering the atmosphere in the two Hemispheres will have 25 times the effect on albedo in the Southern compared with the Northern Hemisphere.

Even when they are emitted in the same areas, there is reason to think that marine DMS emissions may have more climatic impact than the equivalent quantity of sulphur gas emitted from anthropogenic sources. The results of a recent modelling study by Chin & Jacob (1996) are shown in table 1. They show that although in terms of emissions, anthropogenic sources outstrip marine biogenic inputs by 3:1, in terms of column burden (which is

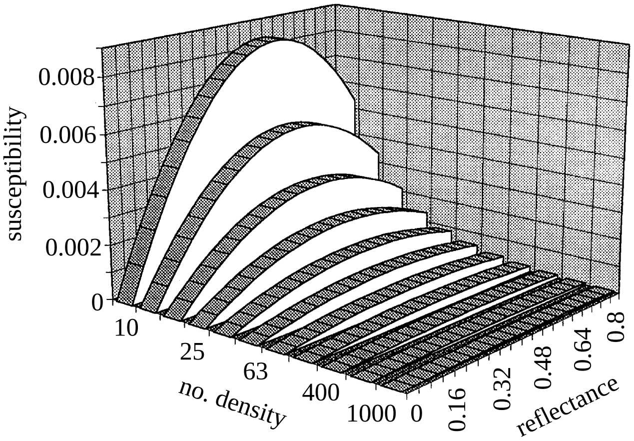


Figure 5. Susceptibility of cloud reflectance to changes in number density of CCN for different total cloud reflectances. Susceptibility is the increase in reflectance per additional droplet cm^{-3}. Redrawn from the equations given by Twomey (1991).

Table 1. *Contributions to the global atmospheric sulphur source and* SO_4^{2-} *burden (from Chin & Jacob 1996)*

	global sulphur source ($\mathrm{Tg\ S\ yr^{-1}}$)	global SO_4^{2-} burden (Tg S)
anthropogenic	67.4 (70%)	0.20 (37%)
biogenic	22.6 (23%)	0.22 (42%)
volcanic	6.7 (7%)	0.10 (18%)
total	96.7	0.53[a]

[a] Oxidation of OCS accounts for 0.016 Tg S (3%), of the global SO_4^{2-} burden, mainly in the stratosphere.

what is important for the formation of CCN) biogenic inputs are just ahead of those from man's activities. This difference arises from the fact that the residence time of the man-made SO_2 is short in comparison with that for DMS, which needs to be oxidized to SO_2 and sulphate before it can be effectively removed from the atmosphere (transformation processes which take tens of hours to several days to occur). The relatively small amount of sulphur from volcanoes also contributes disproportionately to the column burden since, although emitted largely as SO_2, some of this is injected at high altitude which lengthens its atmospheric residence time. It is clear from these arguments that, despite the pervasive influence of man's activities on the global sulphur cycle, marine DMS emissions are potentially still a powerful influence on climate.

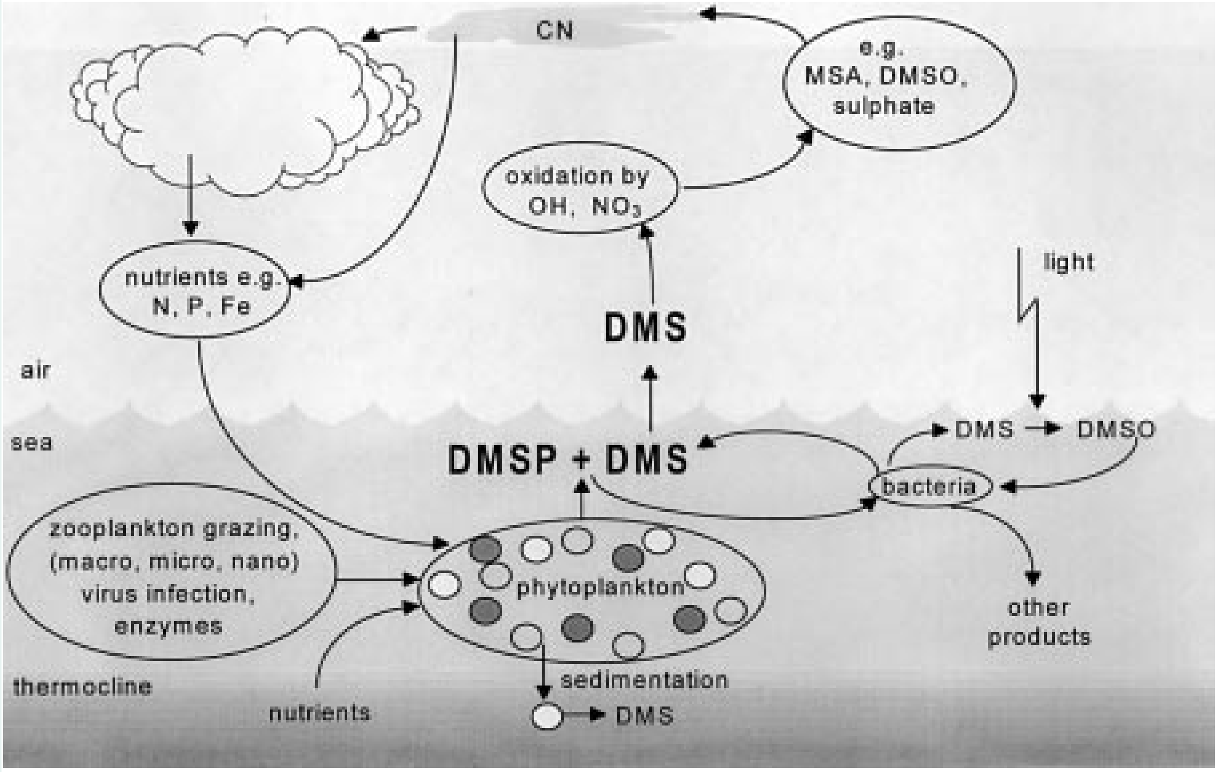
(a) *Factors controlling the production of DMS in seawater*

This is a very large topic which can only be reviewed very briefly here; the interested reader should consult Liss *et al.* (1997) and Malin *et al.* (1994) *inter alia*. The main processes of production and transformation/removal of DMS in the ocean surfaces are shown schematically in figure 6.

Since DMS is formed biologically, the factors controlling its production will be those common to all such processes, i.e. availability of light and nutrients. However, not all phytoplankton have the same ability to form DMSP and hence DMS (Keller 1989; Liss *et al.* 1994). For example, diatoms are poor producers, whereas prymnesiophytes are generally prolific. This is probably because DMSP is made by organisms as an osmolyte and alternative compounds can serve a similar function. One of these is the nitrogen analogue of DMSP, glycine betaine (GBT); and there is some suggestion (Andreae 1986) that plankton can switch between GBT and DMSP depending on the availability of nitrogen in the water (sulphate, from which DMSP is synthesized, is never in short supply). Another nutrient which affects the production of DMS is iron. In the IRONEX I and II experiments in the equatorial Pacific (Martin *et al.* 1994; Coale *et al.* 1996), purposeful addition of soluble iron to a patch of ocean water produced an order of magnitude increase in chlorophyll-*a* levels and a concomitant increase in DMS and DMSP concentrations in the water. The increase in DMS was about threefold; this was significantly less than that for chlorophyll-*a*, and can be attributed to the fact that the main beneficiaries of the iron supplement were diatoms—poor producers of DMS.

Following formation of DMSP and DMS by phytoplankton, the main release to the water comes when the cells senesce and die, or are grazed by zooplankton. Further, the role of viral attack in leading to rapid release of DMS has very recently been described (Malin *et al.* 1998). The conversion of DMSP to DMS both intra- and extracellularly is catalysed by the enzyme DMSP-lyase. The major processes by which DMS is removed/transformed from the water are bacterial and photochemical oxidation to dimethyl sulphoxide (DMSO) and other products, and loss to the atmosphere by sea-to-air exchange. This last mechanism, which is essentially the only one with a direct climatic impact through the sulphur cycle, is thought to be a relatively small 'bleed' in comparison with the internal biological and photochemical flows of S in the water.

Many of the processes mentioned above are subject to alteration as a result of climate change. However, although for some processes the sign of the change is predictable, its magnitude is not, and in some instances even the sign is in doubt. In general, any change which increases marine biological activity (e.g. enhanced nutrient supply from depth due to stronger vertical circulation, increased deposition of iron from the atmosphere arising from stronger winds, or greater aridity on land) will lead to enhanced DMS production and therefore, potentially, to cooling of the atmosphere by increase in cloudiness. However, it is clear that interfering factors, such as the differing abilities of various phytoplankton species to form DMSP/DMS, change in the DMSP:GBT ratio under different N-nutrient regimes, bacterial oxidation of DMS, and the nonlinear atmospheric effects shown in figure 5, amongst others, make quantitative predictions extremely difficult at present. The best guide we seem to have is the historical record from polar ice cores, as discussed below.



re 6. Schematic diagram showing major processes in the cycling of DMS by the marine ecosystem (from Liss *et al.* 1997). See or discussion.

ISCUSSION

Calculation of the present-day global cooling due o the marine biota

O_2

eferring to figure 2, the effect of killing off all the ne biota, over time-scales of a few hundred years, d be to cause atmospheric CO_2 to increase to *ca.* ppm. We use the approximate form for the overall ge in radiative forcing due to CO_2 increases given by ghton *et al.* (1990: their table 2.2), which includes estis of the various mechanisms due to change in water ur and cloud properties, $\Delta F = 6.3 \ln (C/C_o)$ where s the forcing in W m^{-2} and C, C_o are initial and final entrations of CO_2. This suggests a forcing of 3.0 W for a change from pre-industrial (280 ppm) to the ngelove' state, or 5.8 W m^{-2} for the maximum range which the marine biota can modulate the CO_2 entration. Using an average value for the sensitivity e surface temperature in climate models to radiative ng of 1.8 K m^{-2}W^{-1} (Schwartz 1988), we obtain cooldue to the pumpdown of CO_2 by the marine biota of for pre-industrial time, or 3.0 K for glacial time.

DMS

is calculation is more speculative, because of the culty of quantifying how many of the CCNs in the nt atmosphere are derived from marine DMS, and much of the cloud presently in the atmosphere would fected by them. We assume that in the pristine marine sphere the CCN concentration is 400 cm^{-3}, a value d typically today in Southern Hemisphere marine air, and that half of this is due to marine DMS. The amount by which the DMS component changes the albedo of clouds depends on the clouds' thickness. For a typical marine stratus cloud for which the albedo is 40%, the approximate relations given by Twomey (1991), redrawn in figure 5, suggest that doubling the CCN concentration from 200 cm^{-3} to 400 cm^{-3} causes this to increase by 6% to 46%. If approximately one-third of the earth is covered by marine stratus clouds, this would cause a mean albedo increase of *ca.* 2%. The radiative forcing this would cause is $(S/4) \times 0.02$ where S is the solar constant (6.8 W m^{-2}). Using the same sensitivity of temperature to radiative forcing as before, we obtain a value of 3.8 K for the cooling due to present-day DMS production.

The margin of error on this figure is clearly wide: for example, the fraction of the earth covered by marine stratus is difficult to estimate; the figure of one-third (or nearly half of the oceans) is based on the fact that this is the dominant kind of cloud over the sea, and in temperate regions it is the normal state of the marine sky to be covered by such cloud. The estimate that half of the CCN are formed from marine DMS is clearly too high in the Northern Hemisphere today, but is probably conservative for the pristine Southern Hemisphere (Ayers & Gras 1991).

(b) *Glacial–interglacial feedbacks between the marine biota and climate*

The exact causes of the glacial–interglacial changes in atmospheric CO_2 concentration are not known, but the possible contributory mechanisms are reasonably well described. As discussed in §2, these must involve the marine carbon cycle, and many of them involve changes in the HNLC condition in the Southern Ocean. Theoretically possible mechanisms that have been discussed in the literature include changes in the ocean inventory of phosphate and nitrate, and/or changes in the 'Redfield ratios' of these nutrients, allowing the biota to take up more carbon from the surface (Broecker & Peng 1982). Alternatively, changes in ocean circulation, particularly at high latitude, allowing more or less influence of the cold HNLC waters (Siegenthaler & Wenk 1984), or increases in marine biological export production at high latitude (Sarmiento & Toggweiler 1984) could contribute.

Of these, the increase in Southern Ocean export production due specifically to the greater availability of iron as atmospheric dust is particularly appealing. Analysis of dust in the Vostok ice core (Petit *et al.* 1990) indicates that there was considerably more dust in the atmosphere in glacial time, and recent work by Kumar *et al.* (1995) has shown that in the southernmost Atlantic sector at least, this greater flux of iron was accompanied by much greater biological export production. Such production has the capacity, as we have seen, to substantially draw down atmospheric CO_2. If the Ironex II result proves generally applicable to this region, and the result of increased iron supply was that more diatom blooms were produced, it might also have an influence on the global ratio of organic to inorganic carbon in exported material. This is because diatoms produce abundant organic carbon flux to the deep sea, but no inorganic flux: this, as Archer & Maier-Reimer (1994) have shown, would further tend to increase the drawdown of atmospheric CO_2 by increasing the dissolution of calcite carbon from deep-sea sediments.

Turning now to the sulphur cycle, results from an ice core taken at the Vostok station in Antarctica clearly show that in the last glacial period both MSA (which can only be formed by oxidation of DMS) and non-sea salt sulphate (NSSS—the total sulphate less the component arising from sea salt) are higher than now or in the previous interglacial (Legrand *et al.* 1991; figure 7). This is in agreement with the idea that during the last glacial period marine biological activity was enhanced, in important parts of the Southern Ocean at least (Kumar *et al.* 1995). How representative are the Antarctic measurements of conditions worldwide is uncertain. For example, Hansson & Saltzman (1993) present data from a Greenland ice core, which show an apparently opposite trend for MSA but a similar one for NSSS. It is not clear what interpretation we should place on these results, but it seems possible that they tell us more about the behaviour of the branching ratio (which is a measure of how much DMS is oxidized to MSA versus NSSS) than about the level of marine biogenic input of sulphur to the atmosphere. If the trends of DMS production in the two Hemispheres should turn out to be in opposite directions, we might expect that the larger climatic effect would be due to that in the Southern Hemisphere, because of the previously given reasoning concerning the lack of other sources for CCNs in that region.

It therefore seems very likely that, both with respect to CO_2 and DMS interactions, the marine biological changes which occurred across the last glacial–interglacial transition were both positive feedbacks. That is, the glacial condition had higher DMS and lower CO_2, both due to the marine biota, and both of which favoured a colder climate. This supports the idea of an important role for the biota in generating the climatic instabilities which the Pleistocene climate cycles represent (Lovelock & Kump 1994). In the case of glacial time, the important factors then may have been that the climate was drier and also more windy, both being factors which tend to increase the burden of atmospheric dust of terrigenous origin. The drier and colder climate would also have contributed to the lower biological activity on land, so that the glacial–interglacial oscillation may modulate the productivity of the land and marine biota in antiphase to one another.

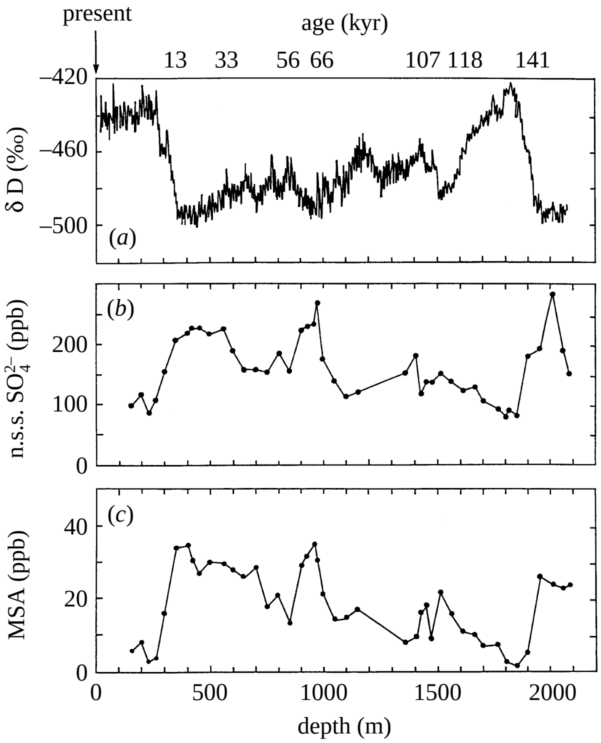


Figure 7. The Vostok ice-core record of (*a*) deuterium concentration (a proxy for local temperature), (*b*) non-sea salt sulphate aerosol, and (*c*) methane sulphonate during the last glacial cycle. After Legrand *et al.* (1991).

5. CONCLUSION: FUTURE CLIMATE CHANGE

Future climate changes such as those presently being brought about by human activities have very different impacts on the linked geochemical cycles of carbon, sulphur and iron than do the glacial–interglacial transitions, and we cannot at present say whether the influence of the marine biota will tend to enhance or diminish anthropogenic climate change over the coming decades and centuries. Most likely, human influence will tend to increase the atmospheric dust burden as a result of agricultural practices (and it is very likely that this is already taking place), and if anything this might be expected to slow global warming according to the arguments given here. Recently, modelling studies reported by Sarmiento & Lequere (1996) of the uptake of CO_2 by the oceans forced by increasing CO_2, have also suggested that the main influence of the marine biota may be a negative feedback, but for a different reason: in some coupled atmosphere–ocean global circulation models, large

gh increases in atmospheric CO_2 cause the global
nohaline circulation to weaken to the point of
pse. This alone slows the absorption of CO_2 by the
ns (i.e. it is a positive feedback on the atmospheric
ease). However, the less vigorous upwelling of deep
r means that the polar HNLC regions contract if the
a are allowed to respond, tending to offset the decrease
ptake. To our knowledge, no similar calculations have
et been carried out to assess the possible consequences
ch changes for release of DMS, but it is clear from our
ussion that this mechanism is likely to have larger
acts over 'human' time-scales than are the mechanisms
lving CO_2.

e end, therefore, deep in the realm of speculation. For
nple, if the DMS–cloud albedo mechanism is found to
s important as simple calculations indicate, the influ-
of changes to the marine biota on climate is likely to
neasurable even over periods as short as a few decades.
ever, our knowledge is as yet insufficient to be confi-
about the magnitude of any such changes, or even
sign. The subject of the marine biota's influence on
ate looks set therefore to continue to be important for
orseeable future in climate research.

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