Ocean carbon-cycle dynamics and atmospheric p_{CO_2}

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Mechanisms are identified whereby processes internal to the oceans can give rise to rapid changes in atmospheric p_{CO_2}. One such mechanism involves exchange between the atmosphere and deep ocean through the high-latitude outcrop regions of the deep waters. The effectiveness of communication between the atmosphere and deep ocean is determined by the rate of exchange between the surface and deep ocean against the rate of biological uptake of the excess carbon brought up from the abyss by this exchange. Changes in the relative magnitude of these two processes can lead to atmospheric p_{CO_2} values ranging between 165 p.p.m. (by volume) and 425 p.p.m. compared with a pre-industrial value of 280 p.p.m. Another such mechanism involves the separation between regeneration of alkalinity and total carbon that occurs in the oceans because of the fact that organic carbon is regenerated primarily in the upper ocean whereas $CaCO_3$ is dissolved primarily in the deep ocean. The extent of separation depends on the rate of $CaCO_3$ formation at the surface against the rate of upward mixing of deep waters. This mechanism can lead to atmospheric values in excess of 20000 p.p.m., although values greater than 1100 p.p.m. are unlikely because calcareous organisms would have difficulty surviving in the undersaturated surface waters that develop at this point. A three-dimensional model that is being developed to further study these and other problems provides illustrations of them and also suggests the possibility that there is a long-lived form of non-sinking carbon playing a major role in carbon cycling.

1. Introduction

The biologically mediated redistribution of carbon and alkalinity within the oceans plays a major role in controlling atmospheric p_{CO_2} and is the most likely cause of changes in this quantity that occur on timescales of a few hundred to a few thousand years. The observation in trapped air bubbles from ice cores that atmospheric p_{CO_2} increased from approximately 200 p.p.m. (by volume) during the last ice age to its pre-industrial value of 280 p.p.m. on a timescale of order 1000 years (Neftel *et al.* 1982) has led to considerable interest in the relevant processes by showing that the system is far more susceptible to rapid change than had been previously thought. Understanding the redistribution processes is of considerable relevance not only to the interpretation of the ice age termination event and other natural events, but also in predicting the global response to the fossil-fuel carbon dioxide transient.

In this paper we discuss our present understanding of the processes determining the carbon and alkalinity distribution, with a particular focus on those that can cause the largest changes in atmospheric p_{CO_2}; we discuss progress towards the development of predictive models; and we discuss some of the important questions concerning our understanding of the carbon and alkalinity cycles in the oceans that are being raised by this work. A first section provides a background discussion, the section following discusses box models that have been developed to

help in identifying those aspects of the carbon cycle to which the atmospheric p_{CO_2} is most sensitive, and a final section preceding the conclusions discusses progress towards the development of three-dimensional models.

2. BACKGROUND

The partial pressure of p_{CO_2} in the oceans is a function of the total carbon concentration, $[\Sigma CO_2]$ and total alkalinity, [ALK]. The key to understanding how biological cycling in the oceans controls atmospheric p_{CO_2} is the fact that vertical profiles of ΣCO_2 and ALK, such as those in figure 1, show a very evident segregation between surface and deep-water masses. The ΣCO_2 and ALK are reduced by organism uptake in the upper euphotic layers of the ocean and are more abundant in the deeper layers where they regenerate. The chemical segregation of these constituents in the oceans leads to an atmospheric p_{CO_2} level that is 3 to 4 times lower than it would be if the oceans were uniformly mixed. In the classical geochemical view, chemical gradients between surface and deep waters are maintained by a balance between the downward flux of sinking biogenic particles and the upward mixing and advection of nutrient, carbon, and alkalinity-enriched deep waters. Sinking particles dissolve or are remineralized in the deep sea, thus closing the cycle. Differences in the regeneration depths of the constituents, which are reflected in the different shapes of the profiles in figure 1, are an important part of the discussion in the next section so are introduced here.
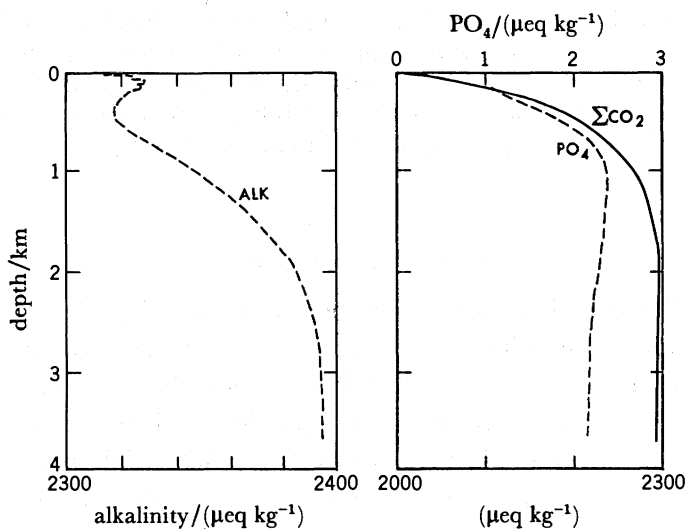

FIGURE 1. Global average profiles of GEOSECS data. Note the deeper regeneration of the alkalinity relative to the total carbon.

In our modelling approach we treat PO_4 interchangeably with nitrate (NO_3) as the nutrient that is limiting to photosynthesis in most regions of the ocean. This is reflected in the fact that the PO_4 concentration is close to zero at the surface (see figure 1). The remineralization in the water column of phosphorus, which is removed from the surface in organic matter, occurs at shallow depths and combines with the circulation pattern to give a maximum in PO_4 concentration at a depth of ca. 1 km.

ALK, on the other hand, varies over a range of less than 5%, and has a broad maximum at about 3 km depth. Its distribution is affected to a small extent by regeneration of organic NO_3, but is dominantly controlled by the cycling of $CaCO_3$ by plankton. Typically, for every mole of PO_4 that sinks out of the surface ocean, there are 15 moles of NO_3, the removal of which increases surface ALK by 15 equivalents, and 32.5 moles of $CaCO_3$ tests, which decrease surface ALK by 65 equivalents. The net decrease in surface ALK is thus 50 equivalents (Takahashi *et al.* 1985). The regeneration of the NO_3 below the surface in the upper part of the water column decreases ALK by 15 equivalents. The dissolution of the $CaCO_3$, which increases ALK by 65 equivalents, occurs at much greater depths in the undersaturated deep ocean by relatively slow processes that are thought to occur primarily after the tests sink to the ocean floor. The effect of biological cycling on ALK is thus to drive its concentration down in the upper ocean both by loss of biogenic material from the surface and regeneration of NO_3 below, and to increase it at depth by dissolution of $CaCO_3$.

The $\sum CO_2$ has a distribution intermediate to ALK and PO_4 because it is present in both organic matter (130 moles of carbon for each mole of PO_4) and $CaCO_3$ (32.5 moles of carbon for each mole of PO_4).

In our modelling work we use the treatment of Takahashi *et al.* (1980) to find the p_{CO_2} at the surface as a function of ALK and $\sum CO_2$. Takahashi's treatment includes dissociation of carbonic acid, boric acid and water. In the range of properties found at the surface, Takahashi's equations predict that the removal of organic matter alone decreases the p_{CO_2}, whereas removal of $CaCO_3$ increases the p_{CO_2}. The net effect of removing $CaCO_3$ on the p_{CO_2} of typical low-latitude water is to increase it by of order 45 p.p.m. (Broecker & Peng 1982). In our treatment discussed below we show that the difference in the regeneration functions of organic carbon and $CaCO_3$ with its consequence of putting ALK deeper down in the water column than $\sum CO_2$, leads to a further increment in surface p_{CO_2} of order 15 p.p.m. A further increase in the separation between these two properties, such as might occur if the deep ocean stagnated, can lead to very large increases in atmospheric p_{CO_2}, as shall be shown below.

3. Box models

Box models are a powerful technique for gaining intuition about how a system functions, and identifying the parameters to which various properties of interest are most sensitive. In doing this it is important that the models developed be simple enough to be readily constrained and interpreted, and that the assumptions made in developing the models and their possible impact be clearly understood. The results from such studies must be viewed with considerable care, as will be shown below by contrasting the results from the two-box model in figure 2 with the models in figures 3 and 5. The model in figure 2 led to an understanding of the carbon cycle in the oceans that suggested only a minimal role for ocean biological cycling and a non-existent role for ocean circulation in leading to changes in $\sum CO_2$ and ALK through time. These conclusions dominated the thinking of many geochemists until the evidence of rapid changes in atmospheric p_{CO_2} at the end of the last ice age forced a major reconsideration and the development of new models.

In developing the box models, our interest is in gaining an understanding of what controls the atmospheric p_{CO_2} level. The upper ocean equilibrates with the atmosphere on a timescale of approximately one year. We therefore seek in every case to find a solution for the surface
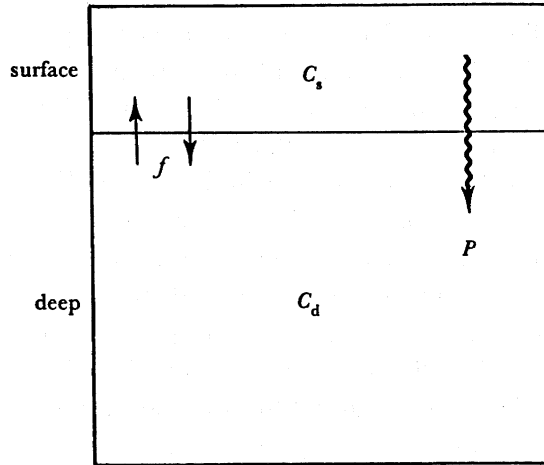
FIGURE 2. A two-box model of the oceans. The f represents physical exchange between the surface and deep box, C_s and C_d represent average surface and deep concentrations, and P represents the particulate rain of phosphate in organic matter. (Taken from Broecker & Peng 1982.)

ocean $\sum CO_2$ and ALK in terms of the minimum number of parameters and concentrations of oceanic constituents. The approach we take is illustrated in detail for the two-box model.

3.1. Two-box model

The two-box model approach is based primarily on the observation that PO_4 is very close to zero over most of the surface ocean. Given this, it does not seem unreasonable to assume that one can treat the surface ocean as a single nutrient depleted box. For the sake of simplicity the deep ocean is treated as another single box (see figure 2), although it is possible, as has been done (Oeschger et al. 1975) to treat it as a stack of boxes. Assuming steady state, one can put down for the deep box, equations of conservation for $\sum CO_2$ and ALK and solve them for the surface values

$$\sum CO_{2_s} = \sum CO_{2_d} - r_{\Sigma CO_2/PO_4} (P/f), \tag{1}$$

$$ALK_s = ALK_d - r_{ALK/PO_4} (P/f). \tag{2}$$

P is the surface new production of PO_4 and the rs are the Redfield ratios of uptake by organisms for the constituents indicated in the subscript. The values of the Redfield ratios have been discussed in §2. A solution for P can be obtained from the PO_4 balance for the surface box

$$P = f(PO_{4_d} - PO_{4_s}). \tag{3}$$

Combining (1) and (2) with (3) and setting PO_{4_s} to 0 gives

$$\sum CO_{2_s} = \sum CO_{2_d} - r_{\Sigma CO_2/PO_4} PO_{4_d}, \tag{4}$$

$$ALK_s = ALK_d - r_{ALK/PO_4} PO_{4_d}. \tag{5}$$

Equations (4) and (5) show that the surface ocean $\sum CO_2$ and ALK, which determine the atmospheric p_{CO_2}, are themselves determined by the deep $\sum CO_2$, ALK, PO_4, and the Redfield ratio of carbon and alkalinity to phosphate in organisms. Broecker (1982) used this model in

his remarkable attack on the problem of the increase of atmospheric $p\mathrm{CO}_2$ that occurred at the end of the ice age. He first collected all the measurements that could provide constraints on the problem, such as the changes in $\delta^{13}\mathrm{C}$ that occurred because of loss of carbon in organic form from the oceans, and the temperature and ocean volume changes. The combined effect of all these changes on atmospheric p_{CO_2} is negligible. He then proposed that the oceanic PO_4 level was reduced by more than one third through deposition onto shelf areas, which were flooded by water when the ice melted. One can readily see from (4) and (5) that such a loss would be associated with an increase in surface $\sum \mathrm{CO}_2$ and ALK, in effect allowing some of the excess carbon stored in the deep ocean to escape to the surface ocean and atmosphere. The net effect on atmospheric p_{CO_2} is to increase it by the required amount. This mechanism requires several thousand years to come to a completion and would be expected to follow the ice melting, rather than preceding it.

The subsequent discovery that changes in the atmospheric p_{CO_2} occurred not once, but apparently many times during the ice ages and that the changes occurred on timescales of a few hundred years (Siegenthaler & Wenk 1984), eliminated the shelf phosphate storage hypothesis from contention. More recent work has suggested that the atmospheric p_{CO_2} changes actually preceded the ice volume changes, rather than being associated with them, as required by the shelf storage hypothesis (Shackleton & Pisias 1985). All of this suggested the possibility of a faster response, and also one that is more sensitive to climate, than any that can occur in connection with major changes in the oceanic reservoirs of the relevant constituents in equations (4) and (5).

A further difficulty with the two-box model is that it is unable to meet some of the most fundamental constraints, such as predicting the deep-ocean oxygen correctly (Sarmiento 1986). The latter problem arises from the fact that deep waters in the ocean originate in high-latitude regions where the higher oxygen solubilities associated with lower temperatures allow the water to carry a heavier oxygen load into the abyss than average surface-ocean water can; and where the nutrients are not depleted. Nutrients that are utilized by organisms sink to the abyss in reduced form and create an oxygen demand. High-latitude outcrop regions send large amounts of oxygen into the abyss without the oxygen demand that would accompany the nutrient depletion that is typical of lower-latitude regions. These observations led to the development of the high latitude outcrop three-box model illustrated in figure 3 and discussed in the following section.

3.2. *High-latitude outcrop three-box model*

The three-box high-latitude outcrop model shown in figure 3 is the next step up in complexity from the two-box model. This model, or simple variants of it, was proposed simultaneously by three groups working independently to explain the ice-age observations (Knox & McElroy 1984; Sarmiento & Toggweiler 1984; Siegenthaler & Wenk 1984). A simple solution for the high-latitude surface $\sum \mathrm{CO}_2$ and ALK can be obtained in a manner analogous to that used in the two-box model:

$$\sum \mathrm{CO}_{2_h} = \sum \mathrm{CO}_{2_d} - r_{\sum \mathrm{CO}_2/\mathrm{PO}_4} (\mathrm{PO}_{4_d} - \mathrm{PO}_{4_h}), \tag{6}$$

$$\mathrm{ALK}_h = \mathrm{ALK}_d - r_{\mathrm{ALK}/\mathrm{PO}_4} (\mathrm{PO}_{4_d} - \mathrm{PO}_{4_h}). \tag{7}$$

A full solution of the model requires equations relating the high-latitude $\sum \mathrm{CO}_2$ and ALK to the low-latitude surface concentrations and atmosphere, but the most important equations are
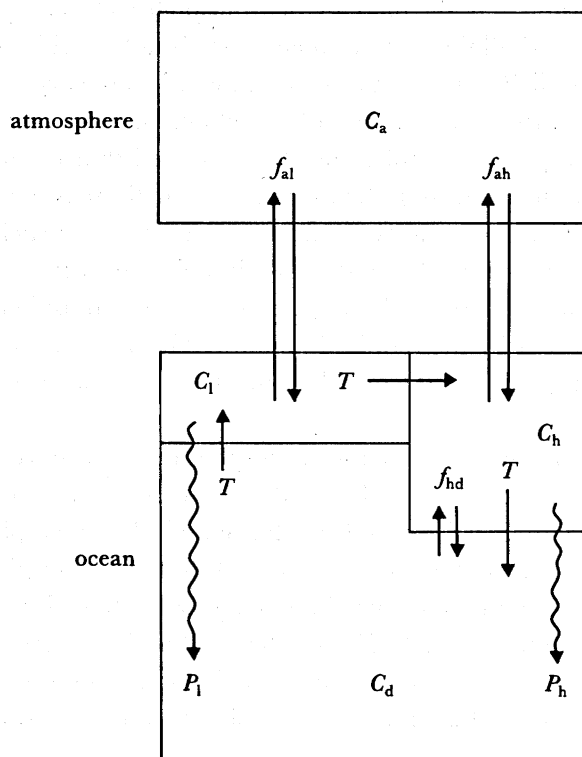
FIGURE 3. A three-box model of the oceans similar to the two-box model in figure 2, only the surface ocean has now been separated into a high-latitude and low-latitude component indicated by the subscripts h and l, respectively. The f_{hd} is exchange between the high-latitude and deep boxes. T represents thermohaline overturning. The Ps are as defined in figure 2. (Taken from Sarmiento & Toggweiler 1984.)

those shown above because the rapid exchange between the deep-ocean and high-latitude box through the f_{hd} exchange term fixes the high-latitude concentrations solidly and allows them to steer the atmospheric and low-latitude concentrations. The full solution, including a description of how radiocarbon and atmospheric p_{CO_2} are used to constrain the parameters, is given in Toggweiler & Sarmiento (1985).

Equations (6) and (7) are virtually identical to (4) and (5) on the right-hand side except for the addition of the PO_{4_h} term. PO_{4_h} can in principle change quite easily. What controls it is a balance between the rate of supply of nutrients to the high-latitude regions by exchange with the deep ocean, and the removal of these nutrients by photosynthetic uptake and sinking. This can be shown by considering the balance equation for the high-latitude box as

$$PO_{4_h} = \frac{PO_{4_d} f_{hd} - P_h}{(f_{hd} + T)}, \tag{8}$$

where we see that an increase in f_{hd} will increase PO_{4_h} and vice versa, and an increase in P_h will decrease PO_{4_h} and vice versa. These changes in PO_{4_h} are linked directly to changes in high latitude ΣCO_2 and ALK through equations (6) and (7), and therefore to atmospheric p_{CO_2}.

In simplest terms what occurs is that the high-latitude box is a window to the deep-ocean carbon excess, with PO_{4_h} as the diagnostic of how open the window is. When PO_{4_h} is high, the

window is open wide and atmospheric p_{CO_2} can increase, as high as 425 p.p.m. from a pre-industrial value of 280 p.p.m. When PO_{4_h} goes down, the window is closed and the atmospheric p_{CO_2} decreases, as low as 160 p.p.m. Figure 4, taken from Sarmiento & Toggweiler (1984) shows the sensitivity to the forcing parameters in more detail.
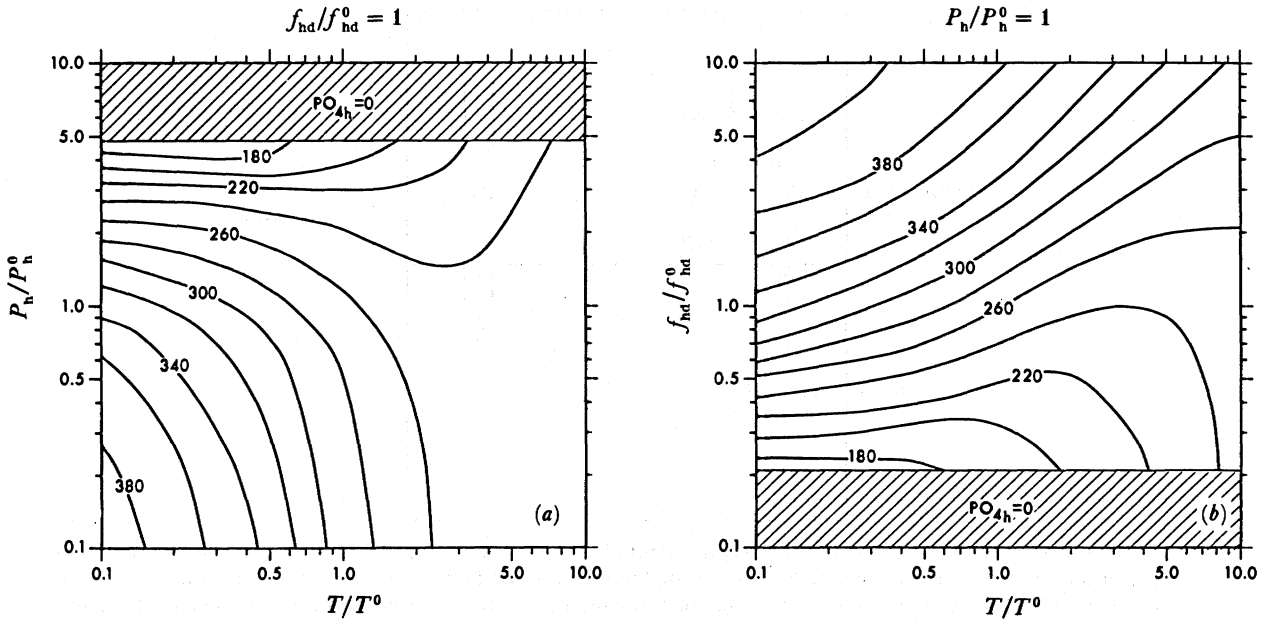

FIGURE 4. Atmospheric p_{CO_2} as predicted by the three-box model for various values of the parameters f_{hd}, P_h, and T. Values $f_{hd}^0 = 38.1 \times 10^6$ m³ s⁻¹, $P_h^0 = 2.31 \times 10^6$ m³ s⁻¹, and $T^0 = 24.5 \times 10^6$ m³ s⁻¹, are obtained by fitting observations of radiocarbon and atmospheric p_{CO_2}. (Taken from Sarmiento & Toggweiler 1984.)

What this model has shown us is that the high-latitude outcrop regions play a central role in controlling atmospheric p_{CO_2} through the rate of nutrient and carbon supply by deep convection relative to the biological uptake of these constituents and their export to the deep ocean. These are processes that might in principle change quite rapidly. A time-dependent solution of the three-box model shows that after an instantaneous perturbation of one of the controlling parameters it takes of the order of 200 years to reach a new equilibrium (Wenk & Siegenthaler 1985). There is also some sensitivity to the overturning T term, although this sensitivity is reduced as one goes to lower atmospheric p_{CO_2} values. It is possible in principle for T, with its associated low-latitude productivity, to vary over a considerable range with only minimal atmospheric p_{CO_2} changes. There is a way, however, in which the low latitudes may affect the atmospheric p_{CO_2}. To understand how this might occur we must turn to yet a different box model.

3.3. Three-stacked box model

One of the first three-dimensional simulations of the carbon cycle that we did, which will be described below, gave surface productivities and atmospheric p_{CO_2} levels that were significantly greater than the present values. From equations (6), (7) and (8) above, we can see that higher productivities should have been associated with lower p_{CO_2}. It quickly became clear that what was occurring in the model was that the high surface productivities, which were caused by the shallow regeneration of PO_4, were giving rise to a large flux of $CaCO_3$ to the deep ocean, which

had the net effect of reducing upper-ocean ALK by trapping it in the deep ocean. Dymond & Lyle (1985) have identified the reverse of this mechanism, triggered by lower productivities, as playing a possible role in the lower p_{CO_2} levels of the last ice age. The three-stacked box model in figure 5 was developed to explore this phenomenon further.
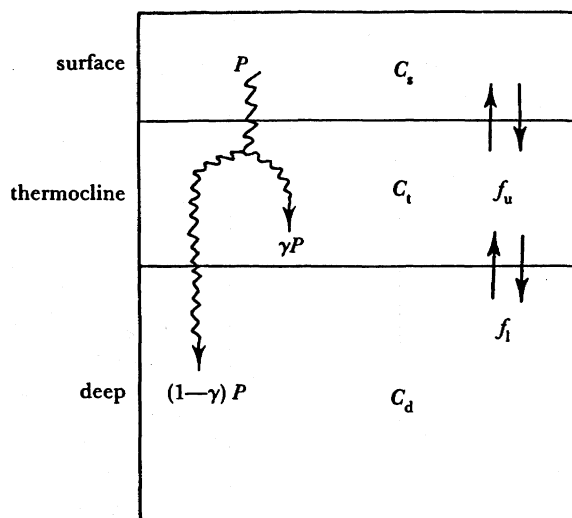

FIGURE 5. A three-stacked box model of the oceans. Symbols are as defined in figure 2; γ represents the fraction of the surface particle production which is regenerated in the middle 'thermocline' box, with the remainder being regenerated in the deep box. We assume that all of the organic matter regenerates in the thermocline box, and that all of the $CaCO_3$ regenerates in the deep box.

Figure 5 shows the three-stacked box model of the ocean. We again take the simplest model possible, this time removing the high-latitude outcrop box (to be returned in the future) and separating the deep ocean into a 'thermocline' box where all of the organic matter produced by organisms is assumed to regenerate, and a deep box where 100% of the $CaCO_3$ is assumed to regenerate. The model is similar to that developed by Dymond & Lyle (1985) in their study, except that instead of f_u they have an overturning term that goes from the surface directly to the deep box and then upwells through the entire water column. A solution for the surface $\sum CO_2$ and ALK in this model is obtained as above:

$$\sum CO_{2_s} = \sum CO_{2_d} - r_{\Sigma CO_2/PO_4} PO_{4_d} \left[\frac{1 + (f_u/f_l)\,(1 - \gamma_{\Sigma CO_2})}{1 + (f_u/f_l)\,(1 - \gamma_{PO_4})} \right], \tag{9}$$

$$ALK_s = ALK_d - r_{ALK/PO_4} PO_{4_d} \left[\frac{1 + (f_u/f_l)\,(1 - \gamma_{ALK})}{1 + (f_u/f_l)\,(1 - \gamma_{PO_4})} \right]. \tag{10}$$

Equations (9) and (10) are again identical to (4) and (5) except for the term in the brackets involving f_u/f_l, the ratio of the upper exchange rate to the lower exchange rate, and the γs. The γs, the values of which can be obtained from the information given in §2, are such that ALK is more sensitive than $\sum CO_2$ to changes in the exchange rate ratio, f_u/f_l. In simplest terms, these equations change atmospheric p_{CO_2} essentially by sequestering or releasing ALK in the deep ocean. Recall that ALK varies inversely with atmospheric p_{CO_2}, thus an increase in the deep-ocean sequestering efficiency or more vigorous surface mixing will lead to an increase in atmospheric p_{CO_2}, and vice versa.

Figure 6 shows the atmospheric p_{CO_2} predicted by this model for various values of the two exchange-rate terms. The atmospheric p_{CO_2} can be driven up to greater than 20000 p.p.m. before the sequestering of ALK in the deep ocean is great enough to drive the surface ALK to 0! Thus, this mechanism has a far greater range on the high end than does the high-latitude outcrop mechanism, but it has very little flexibility on the lower end (of order 15 p.p.m.) because the present level of deep-ocean sequestering of ALK is quite small. It should be noted that in the realm where ALK gets very low, one might expect other components of seawater than carbonic and boric acids and water to play a role in the carbon system speciation, so that Takahashi's (1980) equations, which we have used to calculate the p_{CO_2}, may not apply. However, it would probably be difficult with this mechanism to drive the atmospheric p_{CO_2} any higher than of order 1100 p.p.m., because at this point the surface ocean becomes undersaturated in $CaCO_3$ and the organisms that use $CaCO_3$ in their tests would have difficulty surviving. It is of interest to consider the possibility that a stagnation of the deep ocean might well be associated with extinction events of calcareous organisms and, conversely, that the development of such organisms would require a relatively rapid exchange of the deep ocean with the upper ocean.
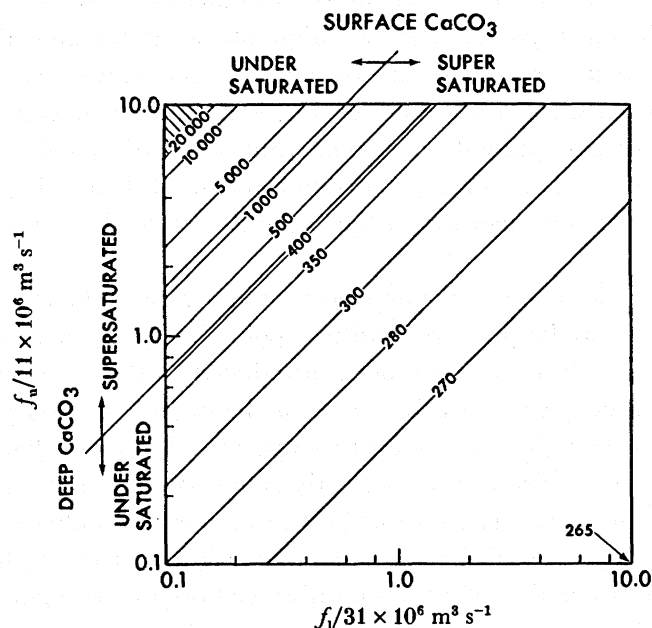

FIGURE 6. Best values for f_u and f_l of 11×10^6 m³ s⁻¹ and 31×10^6 m³ s⁻¹, respectively, were obtained for the model in figure 5 by forcing the model to fit the pre-industrial value of p_{CO_2} (280 p.p.m.) and the deep-ocean pre-bomb radiocarbon average of -160 p.p.t. These values were then varied over an order of magnitude in each direction, as shown. As the atmospheric p_{CO_2} increases, the deep ocean goes from being undersaturated to being saturated, which would sequester $CaCO_3$ even more efficiently by burying it in the sediments, thus driving the model even more rapidly in the direction of higher p_{CO_2} values. Eventually, however, the upper ocean becomes undersaturated, at which point calcareous organisms would have difficulty surviving.

4. THREE-DIMENSIONAL MODEL

The models discussed in the previous section point towards several ways in which changes in processes internal to the ocean, such as the rate and pattern of ocean circulation and of biological cycling, can cause large changes in atmospheric p_{CO_2}. Such models cannot, however,

tell us how those processes would change, nor should the results be entirely trusted unless they can be confirmed with more realistic models or by observations of such changes in the past. In this spirit we are working on the development of integrated models of the ocean carbon system with the major emphasis on understanding how the various processes are related to the physical forcing at the ocean's surface (i.e. the supply of nutrient elements by circulation and mixing, the availability of light, and the dispersion of newly produced material by local turbulence and sinking), as well as chemical and biological regeneration coupled with circulation and mixing in the ocean interior. Such models will eventually be used in conjunction with models of the coupled atmospheric and oceanic circulation to predict the overall response to external perturbations.

At present we have separately developed, or are in the midst of developing, the main components of our series of integrated models. These are: first, the physical-circulation models themselves; second, a one-dimensional model of upper-ocean ecology; third, a model for water-column transformations; and fourth, a sediment-diagenesis model for $CaCO_3$ dissolution to which we will soon add organic carbon oxidation. Our progress in this work is discussed in detail in a technical report (Toggweiler $et\ al.$ 1987).

The production of global integrated models allows us to identify critical unknowns in our knowledge of the ocean's chemical system. When we originally began thinking about modelling chemical fluxes about four years ago, our recipe for making a model was very simple: take a circulation model, add nutrients, convert the surface nutrients into a pool of sinking particles, and remineralize the particles at depth following some scaling law. We found out very quickly, however, that an approach such as this misses important elements of chemical cycling that have much greater consequences for the chemistry of the ocean as well as the atmosphere than we had originally expected.

Our studies have led us to focus on two major aspects of upper-ocean biology that do not fit this simple picture and that may be pressure-sensitive 'points', such as those that have been discussed above. The first, which has already been introduced, is the presence of unutilized nutrients in high-latitude surface water. In these regions the organic carbon production and sinking fluxes are not high enough to deplete nutrients, but the net exchange of O_2 and CO_2 between the atmosphere and deep ocean is greatly enhanced. The work described above has shown us that these regions play a central role in determining atmospheric CO_2 as well as deep-ocean O_2 (Sarmiento & Toggweiler 1984; Toggweiler & Sarmiento 1985).

The second aspect is the production of refractory dissolved organic compounds by marine organisms. We see evidence accumulating that dissolved organic matter (DOM) may be more effective in transporting organic carbon and nutrients out of the upper ocean than particles. We find that the inclusion of DOM in our models can change their behaviour quite dramatically.

In the deep ocean our preliminary studies have led us to focus on the problem of regeneration of $CaCO_3$ and how this affects the distribution of alkalinity. The three-stacked box model discussed above was a direct outcome of some of the results of the work that will be described below.

In what follows we will discuss some results from our first version of a three-dimensional simulation and a two-dimensional version of this. In this model the carbon cycle is parametrized in a very simple fashion, our intention being primarily to begin exploring how the large-scale distributions of ΣCO_2, ALK, and PO_4 can be used to constrain our

understanding of the present ocean, as well as what the role of DOM and of the rate of deep-water formation are in controlling the distribution of these constituents.

4.1. *Model description*

The ocean circulation is predicted by using the primitive equation approach developed by Bryan (1969) for a sector model basin with idealized geometry that is 60° wide and goes from 70° N to 70° S. It has vertical sides and a flat bottom at 4 km with 25 levels in the vertical and 2° horizontal resolution. The wind forcing is the zonally averaged world ocean mean. Temperature and salinity are predicted by using a newtonian damping boundary condition at the surface in which the temperature and salinity are restored towards the zonally averaged Atlantic Ocean data. A similar version of this model is described by Bryan (1986).

The zonally averaged meridional overturning predicted by the model is shown in figure 7. The interior circulation has a much stronger vertical component to it than is obtained with models that have more realistic topography (Bryan & Lewis 1979) or than is generally expected to obtain, although the total deep-water formation rate of order 24×10^6 m^3 s^{-1} is comparable to the Atlantic. The predicted upper-ocean transport has realistic values of Ekman pumping, including strong equatorial upwelling, which is balanced by equatorward transport at depth. The choice of using the model in its present form for these first experiments was made because it is simple and quick to run and because the many experiments carried out by Bryan (1986) have given us considerable familiarity with the behaviour of the model. One of the
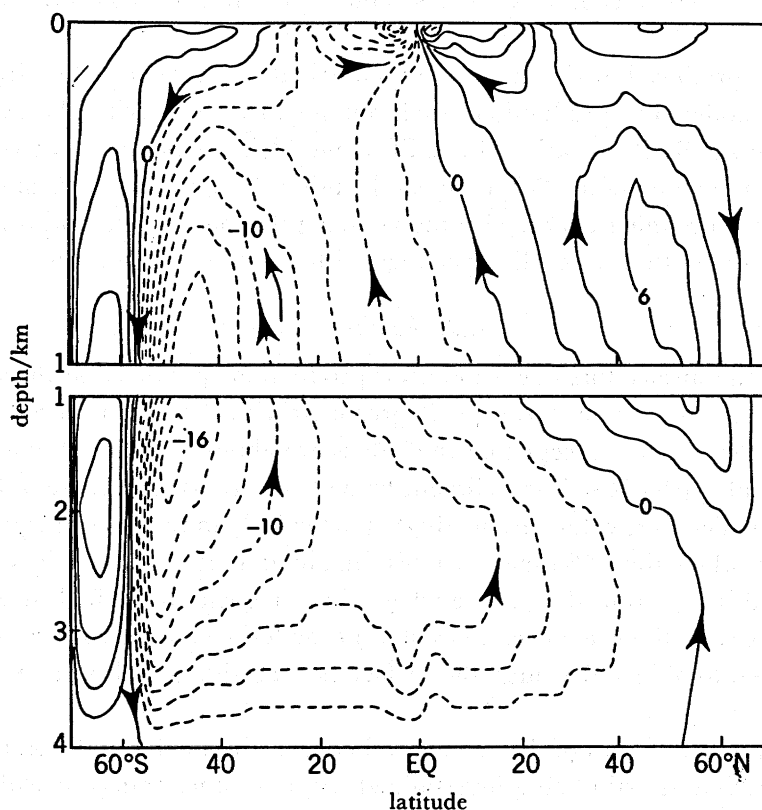

FIGURE 7. The zonally integrated meridional overturning predicted by the three-dimensional sector model described in the text. Units given are 10^6 m^3 s^{-1}.

experiments that we have carried out involves changing the rate of meridional circulation shown in figure 7. The experiments of Bryan (1986) show how this can be done by changing the vertical diffusivity.

The approach we follow in predicting the surface nutrient concentration is essentially the same as for temperature and salinity: the full equation of conservation is solved except for the inclusion of a newtonian damping term of the form $-\gamma([PO_4]-[PO_4^*])$. This term forces the model-predicted PO_4 back towards the observed PO_4^*, which is obtained from GEOSECS observations, thus removing PO_4 from the surface in the process. The model-predicted PO_4 is generally greater than the PO_4^* data because it is continuously supplied from below; γ is the reciprocal of a time constant, which in this case was taken to be 5 days after several experiments.

The PO_4 that is removed from the surface is regenerated in the water column by using a simple scaling law obtained from sediment trap observations (Martin *et al.* 1987), namely:

$$\partial[PO_4]/\partial t = \text{advection} + \text{diffusion} + A\,z^{-1.858}. \tag{11}$$

A is specified for each timestep such that the vertically integrated regeneration for a given geographic location is exactly equal to the nutrient removal at the surface at that location. The assumption implicit in this approach is that the removal of organic matter from the surface occurs primarily by the large particles that are caught in sediment traps. We considered that this was a reasonable initial approach to take, partly because this is the flux term we know most about, and partly because, until we obtained the model results shown below and became aware of some of the most recent work in this area, we considered that this flux term was indeed the major one.

$CaCO_3$, which is produced at the same time as nutrients, is regenerated entirely within the deepest box of the model. The production rate is obtained by multiplying the PO_4 production rate by the appropriate Redfield ratio. The $\Sigma\,CO_2$ and ALK are predicted by removing them from the surface as a function of the PO_4 removal, by using the appropriate Redfield ratios, and then regenerating the organic fraction with the same depth scale as PO_4, and regenerating the $CaCO_3$ fraction in the bottom box. Gas exchange with a uniformly mixed atmospheric box is also included.

4.2. *Results*

Figure 8*a* shows the surface flux of carbon (new production) predicted at the surface by the model. The pattern of production shows good agreement with the primary production map of Koblentz-Mishke *et al.* (1970), except that the values are about an order of magnitude larger than what one would expect based on sediment trap observations. Figure 8*b* of PO_4 at 180 m shows why this is so. The PO_4 values are too high, particularly in the eastern equatorial region where they achieve values almost 3 times greater than any that are observed. These high values are advected and diffused up to the surface where they give rise to the high new production. In later simulations with the same ocean-circulation model, where we succeeded in bringing the PO_4 values down to observed values, the surface new production also came down into the observed range.

What is the cause of these large discrepancies between the model and observations? The answers to this question are still being investigated. Among other things, it will be necessary to carry out simulations with ocean-circulation models that have more realistic meridional overturning. However, our first conclusions are that the increased surface production and
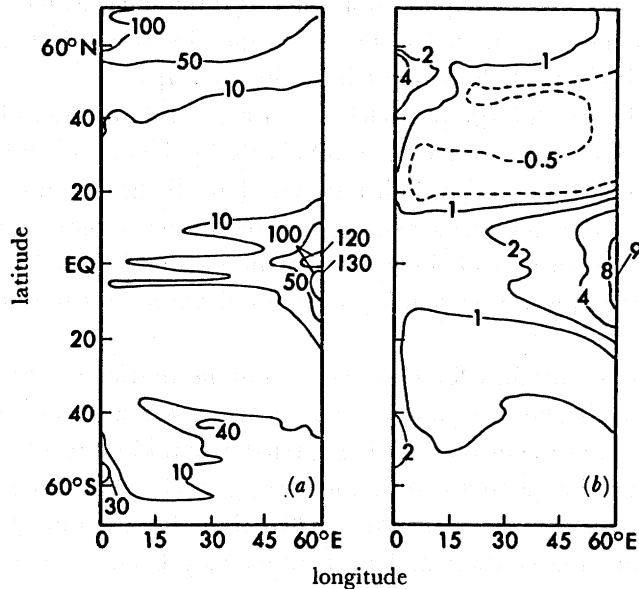
FIGURE 8. (a) Flux of organic carbon predicted by the model in figure 7 at the base of the euphotic zone at 100 m. Units are mole per square metre per annum. The average is 13.4 mol m^{-2} a^{-1}. (b) Phosphate at 180 m as predicted by the model in units of μmole per kilogram.

PO$_4$ result from an incorrect characterization of the cycling of organic matter in the oceans. This explanation is explored in what follows.

The major differences between the PO$_4$ field predicted by the model and the observed PO$_4$ field are that the model concentrations are too high, and that the zonally averaged nutrient maximum, which is at approximately 400–500 m at the Equator in the model, is too shallow by about 500 m. Our model is very efficiently trapping nutrients in the upper part of the water column, particularly in the tropics. Such trapping is a normal characteristic of regions where the waters transported away from the trapping region have their nutrients removed very efficiently before they can escape the region, and where the waters flowing in to the region trap along the way the nutrients that are removed from the outflowing waters. In a steady state, such as we have assumed, the inflow of nutrients must balance the outflow, but it may take very large concentrations within the trapping region to provide enough nutrients to the outflowing waters in order to balance the inflowing nutrient flux. The equatorial upwelling regions have these characteristics, in that the outflowing water is at the surface, where organisms can very effectively remove nutrients, whereas the inflowing waters are in the thermocline where most of the nutrients are regenerated. Our model is an example of this naturally observed phenomenon that has gone to an extreme.

The regeneration function that was used for organic matter in our first experiment (equation (11)) is obtained from observations of the decrease with increasing depth of material caught in sediment traps (Martin *et al.* 1987). The flux decreases to 1/e at a distance of 220 m below the 100 m base of the euphotic zone. This can be compared to the 1/e scale depth of 340 m obtained by Jenkins (1982) from his oxygen-utilization rate estimates, and 400 m obtained also from oxygen observations by Wyrtki (1962). Not only is the sediment trap scale depth smaller but, as Martin *et al.* point out, their power-law function gives a more rapid drop off than the exponential fits of the other investigators such that the latter have much more regeneration

occurring in deeper waters. A likely explanation for this difference, which we explore below, is that organic carbon is being removed from the surface in forms that are regenerated at greater depths than the large particles caught in sediment traps.

Sediment traps typically catch large particles which have sinking rates of order 100 m d^{-1}. Such materials sink too rapidly to be affected significantly by the oceanic advection field. This is implicit in our modelling approach, which requires that all the organic matter (as well as the $CaCO_3$) that is produced at the surface be regenerated in the water column directly below. Note that the rapid sinking rates and short regeneration scale depths of the large particles caught in sediment traps imply an extremely short timescale for regeneration of these large particles.

Other materials that may account for removal of organic matter produced in the surface, such as small particles, or dissolved organic matter (DOM), either sink very slowly or not at all and would therefore be more susceptible to being carried around by the advection field, if their regeneration timescales are longer than those for large particles. The recent observations by Suzuki et al. (1985) and Sugimura & Suzuki (1988), that the amount of DOM in the water column appears to be far greater than had been previously been measured, have led us to investigate the possibility that DOM transport and regeneration may account for the difference between the model and observations.

To carry out a larger number of investigations, our three-dimensional model was zonally averaged and reincarnated as a two-dimensional model. This model predicted the PO_4 and surface productivities shown in figure 9a. The problem of high PO_4 in the equatorial region is worse in the two-dimensional model than in the three-dimensional model primarily because of the absence of the inflow of low PO_4 waters in the Equatorial Undercurrent. The PO_4 maximum is thus shallower and larger than the zonal average of the three-dimensional model. This model predicts a very high p_{CO_2} of 620 p.p.m. because of the strong driving, by the high surface production predicted by the model, of the alkalinity pump mechanism explored above with the three-stacked box model.

Figure 9b shows the result of a two-dimensional simulation in which half the surface production of organic matter was put into DOM, which was then allowed to diffuse and advect. The regeneration time of the DOM was set at 166 years by requiring that the DOM inventory match the observations of Sugimura & Suzuki (1988). The results in figure 9b are greatly improved. The nutrient maximum has moved down to a more appropriate depth and has been reduced to a more realistic value. The production of DOM with a long regeneration time allows the nutrients brought into the equatorial region by upwelling and taken up by organisms to escape from the region by surface Ekman transport and participate more fully in the large-scale circulation patterns before being regenerated.

Another way in which the results of the model are improved by including DOM is that the atmospheric p_{CO_2} now falls to a value of 308 p.p.m. from the value of 620 p.p.m. predicted by the non-DOM case. This is because of the cycling of $CaCO_3$. In the model without DOM, the high upper-ocean productivities are equivalent to increasing f_u relative to f_i in the three-stacked box model described above. The high surface productivities shuttle unusually large amounts of $CaCO_3$ to the deep ocean, thus reducing the surface alkalinity and giving rise to the exceptionally high atmospheric p_{CO_2} levels obtained. With normal upper-ocean productivities the ocean is able to bring the deep waters up with sufficient efficiency that the atmospheric p_{CO_2} can be kept within normal levels.
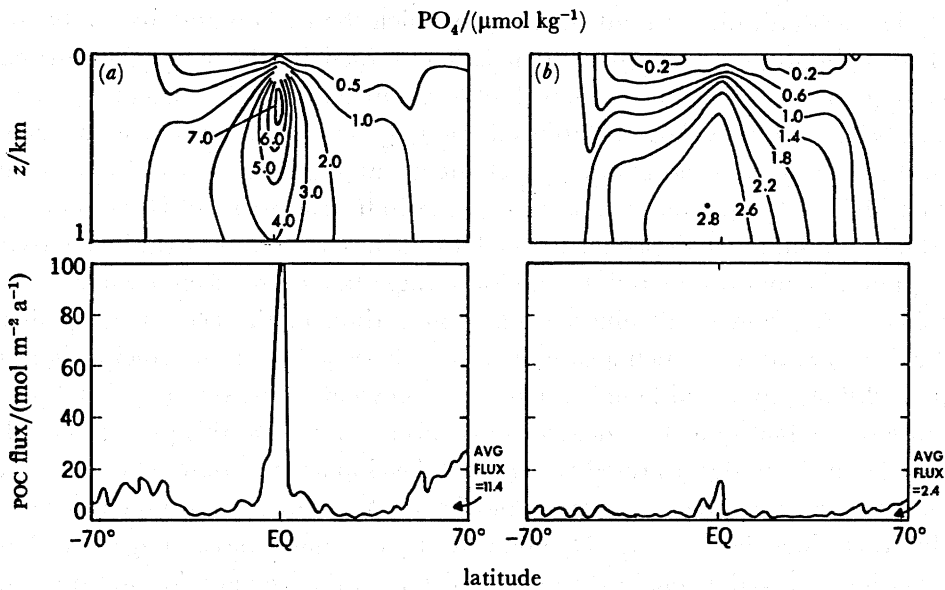
PO$_4$/(μmol kg^{-1})

FIGURE 9. (a) Phosphate in the upper 1000 m, and particulate organic carbon flux (POC) predicted by a two-dimensional model obtained by zonally averaging the three-dimensional model in figure 7. (b) The same figures for a version of the two-dimensional model in which half of the organic carbon production is put into the form of dissolved organic matter with a regeneration timescale of 166 years.

There are other possible explanations for our nutrient trapping problem. The role of the circulation, which has been alluded to above, needs to be investigated. Simply increasing the regeneration scale depth of the sinking material helps as well, but it needs to be kept in mind that the scale depths we use are observationally based. We prefer to take as a working assumption that the scale depth used is appropriate for the large particles and to consider, as we have, what other constituents may be involved in the removal of organic matter from the surface.

Finally, another aspect of the problem that has not been discussed here is the role of oxygen. At PO$_4$ levels much above about 3 μmol kg^{-1} the cumulative oxygen demand is great enough that most waters are at or near anoxia. Under such circumstances the oxidation of organic matter ceases. When we include a prediction of oxygen in our model the entire region under the Equator goes anoxic and the organic matter falls below the anoxic region before it is regenerated, thus in effect lengthening the regeneration scale depth. The PO$_4$ concentrations predicted in this case are comparable to those observed in the oceans, but the oxygen is not, in that the regions where anoxia is present in the oceans are more limited than those predicted by the model. It is apparent from this that oxygen also provides a strong constraint on the model that needs to be considered.

5. CONCLUSION

The studies we have carried out show that the oceanic carbon cycle is far more dynamic than had previously been thought, responding, as it does, to the pattern and magnitude of ocean circulation as well as to the biological productivity. We have identified two major mechanisms internal to the oceans that may lead to significant changes in atmospheric p_{CO_2} on timescales as short as of order 200 years. One involves the high-latitude processes that govern the exposure of the atmosphere to the carbon-enriched deep waters. The diagnostic of the extent of contact

that we use is the high-latitude nutrient content, to which the carbon and alkalinity contents are linked. The high-latitude nutrient content is determined by the supply of nutrients by physical exchange processes against removal of the nutrients by biological uptake. This mechanism has been used to explain the atmospheric p_{CO_2} increase that occurred at the end of the ice age and may lead to atmospheric p_{CO_2} changes ranging from a low of approximately 165 p.p.m. to a high of 425 p.p.m. compared to a pre-industrial value of 280 p.p.m.

The second mechanism involves primarily low-latitude processes and might be referred to as the alkalinity pump. Higher productivities and/or a stagnation of the deep ocean can give rise to an increasing segregation of alkalinity from total carbon in the oceans, with alkalinity trapped in the deeper waters. In such a case the atmospheric p_{CO_2} can, in principle, go as high as greater than 20000 p.p.m., although an increase beyond approximately 1100 p.p.m. is unlikely because of the fact that the calcareous organisms that drive this process would have difficulty surviving in the undersaturated waters that develop at this point. The segregation at present is small and so it is difficult for the atmospheric p_{CO_2} to be taken much below about 265 p.p.m. by reversing the process. Dymond & Lyle (1985) have suggested that this mechanism may have played a role in the decreased p_{CO_2} of the ice ages. We are interested in exploring whether it may have played a role in the more distant past.

Our first experiments with development of two-dimensional and three-dimensional models of the carbon cycle to further study processes such as the above have led to some very interesting results that are consistent with various observational constraints suggesting that the interior recycling of carbon in the oceans may involve significant contributions from refractory materials capable of being carried great distances from their point of formation. DOM is suggested as the culprit, although the work is far from conclusive.

REFERENCES

Broecker, W. S. 1982 *Geochim. cosmochim. Acta* **46**, 1689–1705.
Broecker, W. S. & Peng, T.-H. 1982 *Tracers in the sea.* (634 pages.) Palisades, New York: Eldigio Press.
Bryan, F. 1986 *Maintenance and variability of the thermohaline circulation.* Ph.D. thesis, Princeton University, Princeton, New Jersey.
Bryan, K. 1969 *J. Computat. Phys.* **4**, 347–376.
Bryan, K. & Lewis, L. J. 1979 *J. geophys. Res.* **84**, 2503–2518.
Dymond, J. & Lyle, M. 1985 *Limnol. Oceanogr.* **30**, 699–712.
Jenkins, W. J. 1982 *Nature, Lond.* **300**, 246–249.
Knox, F. & McElroy, M. B. 1984 *J. geophys. Res.* **89**, 4629–4637.
Koblentz-Mishke, O. J., Volkovinsky, V. V. & Kabanova, J. G. 1970 In *Scientific exploration of the South Pacific* (ed. W. S. Wooster), pp. 183–193. Washington, D.C.: National Academy of Sciences.
Martin, J. H., Knauer, G. A., Karl, D. M. & Broenkow, W. W. 1987 *Deep Sea Res.* **34**, 267–286.
Neftel, A., Oeschger, H., Schwander, J., Stauffer, B. & Zumbrunn, R. 1982 *Nature, Lond.* **295**, 220–223.
Oeschger, H., Siegenthaler, U., Schlotterer, U. & Gugelman, A. 1975 *Tellus* 2, 168–192.
Sarmiento, J. L. 1986 In *The role of air–sea exchange in geochemical cycling* (ed. P. Buat-Menard), pp. 65–82. New York: D. Reidel Publishing.
Sarmiento, J. L. & Toggweiler, J. R. 1984 *Nature, Lond.* **308**, 621–624.

Shackleton, N. J. & Pisias, N. G. 1985 In *The carbon cycle and atmospheric CO_2: natural variations archean to present* (ed. E. T. Sundquist & W. S. Broecker), vol. 32 (Geophysical Monograph Series), pp. 303–318. Washington, D.C.: American Geophysical Union.

Siegenthaler, U. & Wenk, T. 1984 *Nature, Lond.* **308**, 624–626.

Sugimura, Y. & Suzuki, Y. 1988 *Mar. Chem.* (In the press.)

Suzuki, Y., Sugimura, Y. & Itoh, I. 1985 *Mar. Chem.* **16**, 83–97.

Takahashi, T., Broecker, W. S., Bainbridge, A. E. & Weiss, R. F. 1980 *Carbonate chemistry of the Atlantic, Pacific, and Indian Oceans: the results of the Geosecs expeditions, 1972–1978,* Tech. Rep. 1, CU-1-80, Lamont-Doherty Geol. Obs., Palisades, New York.

Takahashi, T., Broecker, W. S. & Langer, S. 1985 *J. geophys. Res.* **90**, 6907–6924.

Toggweiler, J. R. & Sarmiento, J. L. 1985 In: *The carbon cycle and atmospheric CO_2: natural variations archean to present* (ed. E. T. Sundquist & W. S. Broecker), vol. 32 (Geophysical Monograph Series), pp. 163–184. Washington, D.C.: American Geophysical Union.

Toggweiler, J. R., Sarmiento, J. L., Najjar, R. & Papademetriou, D. 1987 *Models of chemical cycling in the oceans.* Ocean Tracers Laboratory Technical Report no. 4, Princeton University, Princeton, New Jersey.

Wenk, T. & Siegenthaler, U. 1985 In *The carbon cycle and atmospheric CO_2: natural variations archean to present* (ed. E. T. Sundquist & W. S. Broecker), vol. 32 (Geophysical Monograph Series), pp. 185–194. Washington, D.C.: American Geophysical Union.

Wyrtki, K. 1961 *Deep Sea Res.* **8**, 39–64.

Discussion

D. J. WEBB (*Institute of Oceanographic Sciences, Wormley, Godalming, Surrey, U.K.*). The three-box model showed that both the thermohaline circulation and the vertical mixing at high latitudes affected the flux of CO_2 into the deep ocean. Sedimentary evidence indicates that the thermohaline circulation changed significantly during recent ice ages. Can Professor Sarmiento therefore say what levels of CO_2 are predicted by the model as being possible caused by changes in just this one term?

J. L. SARMIENTO. The three-box model parameter T, which we have referred to as the thermohaline overturning term, can affect the CO_2 level by greater than 100 p.p.m., although the sensitivity to this term diminishes greatly as one approaches the low CO_2 levels of the last ice ages (see figure 4). The 'vertical mixing' term, f, which we have characterized as being in some ways equivalent to Antarctic Bottom Water Formation, is thus probably the most important one to study. It should be pointed out that f must also involve significant lateral exchange within the ocean basins. Therefore much of the evidence that exists for changes in water-mass distribution is relevant to this term as well as to T.

W. J. JENKINS (*Woods Hole Oceanographic Institution, Woods Hole, U.S.A.*). Could not the unrealistically large 'new production' and subsequent anoxia and anomalous phosphate distributions in Professor Sarmiento's model be ameliorated by a choice of a longer vertical scale length for his remineralization function? In particular, I have in mind the kind of vertical attenuation rates observed by myself in subtropical gyre oxygen-utilization rates. By depositing the remineralized nutrients in deeper strata that will have characteristically longer return timescales, one should deepen the nutrient maxima and slow down new production rates.

J. L. SARMIENTO. We have done several experiments where the vertical scale length of regeneration was increased. The results, although an improvement, were not as satisfactory as those obtained with the dissolved organic matter experiments. In our model it appears to be necessary that a mechanism exist that allows the organic matter to be advected and diffused

horizontally away from where it is produced. The difference in vertical scale length between Dr Jenkins's oxygen-utilization rate results and the sediment-trap results provides strong support for the idea that there is some organic matter which is not being caught by the sediment traps, but it does not carry direct information about what form that organic matter should take. Our model provides at least some suggestive evidence that it must be something that can be advected and diffused.

C. WUNSCH (*Center for Meteorology and Physical Oceanography, Massachusetts Institute of Technology, U.S.A.*). Would Professor Sarmiento comment on the issue of whether the biogeochemical results of a model should be taken seriously when the model is known to have serious physical shortcomings? This question is stimulated by his reference to Toggweiler's results.

J. L. SARMIENTO. 'Toggweiler's results', by which I believe Professor Wunsch means the three-dimensional model study, are actually Najjar's results. Yes, I do believe that the biogeochemical results should be taken seriously, otherwise we would not be taking this approach! We are trying to understand the basic mechanisms underlying the carbon cycle so that we can predict the response of the globe to perturbations in this cycle. The particular model we are working with has the advantage of being inexpensive to run, and of being well understood, in that Bryan (1986) has done a detailed study in a model similar to it of what controls the rate of thermohaline overturning. One of our major goals in working with this particular model is to take advantage of Bryan's work to carry out a series of experiments to test out the ideas we have developed concerning the role of high latitude deep water formation in controlling atmospheric CO_2.

Our serendipitous finding about the importance of the role of some refractory form of organic matter in carbon cycling is a good example of the usefulness of the approach we are taking. We do not feel we can conclude based on the model alone that there is a need for a refractory carbon source, but we do feel that the model points towards the possible major impact of having such a source. More realistic ocean-circulation models, which are far more expensive to run, are available and will be used when we have a better understanding of how to simulate the carbon cycle.

H. ELDERFIELD (*Department of Earth Sciences, University of Cambridge, U.K.*). The vertically stacked three-box model that Professor Sarmiento has described has similarities in principle to the 'rain ratio model' where differences in the ratio of organic to inorganic carbon flux between the deep sea and the margins (principally upwelling régimes) allow changes in coastal productivity to affect the CO_2 system between glacial and interglacial times. Has Professor Sarmiento considered lateral exchange in his models, in particular those that consider the role of ocean margins?

J. L. SARMIENTO. No, we have not considered lateral exchange, but clearly this is something of great importance that we need to do.

M. WHITFIELD (*Marine Biological Association, Plymouth, U.K.*). General circulation models of the atmosphere suggest that increases in atmospheric temperature associated with the CO_2 'greenhouse effect' will be accompanied by a decrease in the temperature gradients from

Equator to Pole. One would naïvely assume that this would result in a slowing down of the ocean circulation. Are we in a position to predict the 'sign' of the associated p_{CO_2} changes? Will a positive feedback effect result?

J. L. SARMIENTO. Interestingly, the work of Manabe & Bryan suggests that the rate of deep-water formation does not change with increasing CO_2. This is explained as being caused by the fact that the north–south ocean density does not change significantly with the warming. The density of seawater is not very sensitive to temperature in the high latitudes and salinity changes tend to compensate for whatever density changes do occur. If the deep-water formation did slow down, the three-box model predicts that the equilibrium atmospheric CO_2 would drop, thus giving a negative feedback. However, in a non-steady state this needs to be balanced against the slow down in uptake of the fossil-fuel CO_2 excess.

Reference

Manabe, S. & Bryan. K. 1985 *J. geophys. Res.* **90**, 11689–11708.

J.-F. MINSTER (*CNES/GRGS, Toulouse, France*).
1. In the three-dimensional model, in addition to possible difficulties related to the circulation pattern and the redissolution function, there might be problems because of the forcing parameter of surface phosphate concentration. This parameter is significantly smaller (time delay larger) in tropical oceans compared with higher latitudes. This could lead to the calculation of too-large productivities.
2. In the stacked three-box model, it is not clear whether carbonate redissolution from the sediments, when the diffusion parameters are changed, is well taken care of. It seems to me that this process should prevent the surface layer from taking very low ΣCO_2 and ALK values.

J. L. SARMIENTO.
1. It is tempting but incorrect to try and relate the time constant in our newtonian damping term to the actual timescale of the biological response to a change in nutrient concentration. By analogy with the use of the equivalent boundary condition often used in predicting temperature in primitive equation models, if one is restoring towards the temperature in the atmosphere above the ocean, then one should use a timescale that relates to the physical processes of heat exchange. However, if one is restoring towards the observed ocean temperature, then the appropriate restoring time is infinitely small, or as small as the timestep allows. Our nutrient model is equivalent to the latter case.
2. The effects of carbonate dissolution have not been simulated explicitly in our models, but our calculations of the carbonate saturation levels supports Dr Minster's point. When atmospheric CO_2 levels near 1100 p.p.m., calcium carbonate becomes undersaturated in the surface box. This has two consequences: firstly, the dissolution of shallow calcareous sediments would provide a strong buffer to any further CO_2 changes; and secondly, calcareous organisms would probably not even survive under such conditions so that the alkalinity pump would most likely cease.