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A PRELIMINARY MODEL OF THE ROLE OF UPPER OCEAN CHEMICAL DYNAMICS IN
DETERMINING OCEANIC OXYGEN AND ATMOSPHERIC CARBON DIOXIDE LEVELS

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ABSTRACT

A first version is presented of equations for a three-dimensional model of nutrient and carbon cycling in the oceans. An analytical solution of these equations has been obtained for a one-and-a-half-dimensional "pipe" model. This solution shows that atmospheric CO_2 can be varied by changing the level of preformed nutrients. It is suggested that this mechanism may explain the lower $p\text{CO}_2$ values of the last ice age.

INTRODUCTION

We are in the process of developing a three-dimensional model of nutrient cycling in the oceans. The development of such a model is a two part task requiring the development of ocean circulation models as well as the development of techniques for parameterizing biological and chemical processes. The ocean circulation models that will be used for this study are tracer-calibrated primitive equation models of the type first developed by Bryan (1969). Sarmiento (1983) has described some of the tracer calibration work that is being done with these types of model. This brief account describes our preliminary ideas on how to parameterize the biological and chemical processes. Solutions will be given for a simple one-and-a-half-dimensional model. An analysis of these solutions reveals that atmospheric CO_2 concentrations and oceanic O_2 concentrations are strongly affected by the level of preformed nutrients in deep water. A new mechanism is suggested for the glacial to interglacial increase of atmospheric CO_2 which requires a change in the level of preformed nutrients. This new mechanism does not demand the massive changes in oceanic total carbon alkalinity, and phosphate, required by the Broecker (1982) hypothesis.

This work was completed by mid July 1983. More recent results have since appeared (Sarmiento and Toggweiler, 1984; Toggweiler and Sarmiento, 1985) and related work by other groups has also been published (Siegenthaler and Wenk, 1984; Knox and McElroy, 1984; Wenk and Siegenthaler, 1985; Ennever and McElroy, 1985).

A full description of these equations with appropriate attributions will be given in a future paper by Toggweiler and Sarmiento. We owe a great deal to a variety of studies such as those using sediment traps, on trace metals and radionuclides, particularly thorium (e.g., Bacon and Anderson, 1982), nutrient modeling studies such as that of Wyrтки (1962) and Grill (1970), and the investigation of the Narragansett estuary by Kremer and Nixon (1978).

The work on thorium and sediment traps suggests the possibility of treating particles as if they had a bimodal size distribution: small non-settling particles and large fast-settling particles. There is also a need for a means of changing one kind of a particle to another, namely, zooplankton. We thus have three equations governing particulates and animals:

$$\frac{\partial A}{\partial t} = \alpha(g_s P_s + g_l P_l) - RPA(T) \cdot A + ADV/DIFF \tag{1}$$

$$\begin{aligned} \frac{\partial P_l}{\partial t} = & \beta(1 - \alpha)(g_s P_s + g_l P_l) - RPL(T) \cdot P_l \\ & - g_l P_l - \omega_L \frac{\partial P_l}{\partial z} + ADV/DIFF \end{aligned} \tag{2}$$

$$\begin{aligned} \frac{\partial P_s}{\partial t} = & (1 - \beta)(1 - \alpha)(g_s P_s + g_l P_l) - RPS(T) \cdot P_s \\ & - g_s P_s + ADV/DIFF \end{aligned} \tag{3}$$

Animals "graze" small and large particles at rates g_s and g_l , respectively. They convert these into biomass with an efficiency α . Of the remaining material, a fraction β is expelled as large particles, and a fraction $(1 - \beta)$ is expelled as small particles. They metabolize at a rate $RPA(T)$, and the temperature dependence of this rate may be included if desired. Bacteria metabolize small and large particles at rates $RPS(T)$ and $RPL(T)$, respectively. Large particles also fall through the water column at a speed ω_L .

The advection-diffusion terms take the form

$$ADV/DIFF = \vec{V} \cdot (K \vec{\nabla} P) - \vec{V} \cdot \vec{\nabla} P \tag{4}$$

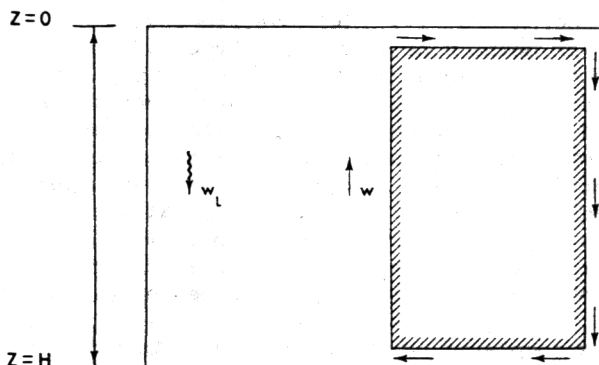


Fig. 1. Schematic diagram of "pipe" model discussed in text.

Solutions to these equations can be readily obtained if one ignores advection/diffusion and assumes steady state:

$$A = \frac{\alpha}{RPA(T)} (g_s P_s + g_L P_L) \quad (5)$$

$$P_s = \frac{(1 - \alpha)(1 - \beta)g_L P_L}{RPS(T) + g_s[1 - (1 - \alpha)(1 - \beta)]} \quad (6)$$

$$P_L = P_L^0 e^{-az} \quad (7)$$

where

$$a = \frac{RPL(T) + g_L}{\omega_L} - \frac{\beta(1 - \alpha)}{\omega_L} g_L \frac{RPS(T) + g_s}{\{RPS(T) + g_s[1 - (1 - \alpha)(1 - \beta)]\}}$$

The constant P_L is the large particle concentration at the surface. The distribution of "animals" and small particles is controlled by the shape of the large particle curve, which is exponential. The scaling length for the large particles, $1/a$, is estimated by us to be of the order of 300 m, from sediment trap measurements (e.g., Knauer et al., 1979; Knauer and Martin, 1981). It should be noted, however, that "a" contains many terms that may not be independent of depth. We have included explicitly the possible dependence of respiration rates on temperature. Suess (1980) has discussed evidence from sediment traps that is consistent with a decrease in "a" with increasing depth. We could get the same result by assuming a decrease with depth of respiration or grazing (or both) of large particles. A decrease in either would be consistent with the sign of the temperature dependence (Kremer and Nixon, 1978).

The phosphate conservation equation is:

$$\frac{\partial PO_4}{\partial t} = r_{PO_4:C}(RPA(T) \cdot A + RPS(T) \cdot P_s + RPL(T) \cdot P_L) - r_{PO_4:C} \cdot \text{FIXATION} + \text{ADV/DIFF} \quad (8)$$

where $r_{PO_4:C}$ is the Redfield ratio of phosphate to carbon in organisms. The fixation term will not be discussed here. We plan to use a formulation similar to that of Kremer and Nixon (1978), which includes the effects of light, nutrient supply, and temperature.

The oxygen equation is:

$$\frac{\partial O_2}{\partial t} = -r_{O_2:C}(RPA(T) \cdot A + RPS(T) \cdot P_s + RPL(T) \cdot P_L) + r_{O_2:C} \cdot \text{FIXATION} + \text{GAS EXCHANGE} + \text{ADV/DIFF} \quad (9)$$

where $r_{O_2:C}$ is the oxygen to carbon ratio in organisms. The other terms are as explained above.

Solutions to the oxygen and phosphate equations have been obtained for the "pipe" model depicted in Fig. 1. It is assumed that the vertical eddy diffusivity, K , and the vertical advection, ω , are constant everywhere. The flux of phosphate into the surface by mixing is balanced by a loss of phosphate in large particles. The flux of large particles into the bottom is balanced by an upward flux of phosphate. The pipe has the same concentration as the surface.

The solutions are:

$$PO_4 = PO_{4s} + \frac{(\overline{PO_4} - PO_{4s}) H (e^{\frac{\omega}{K}z} - e^{-az})}{\left[\frac{K}{\omega} (e^{\frac{\omega}{K}H} - 1) + \frac{1}{a} (e^{-aH} - 1) \right]} \quad (10)$$

where $(\overline{PO_4}) = \left[\int_0^H PO_4 dz \right] / H$

$$O_2 = O_{2s} - r_{O_2:PO_4} (PO_4 - PO_{4s}) \quad (11)$$

The form of the equations is equivalent to what one would obtain by assuming that respiration decreases exponentially with depth with a scale length $1/a$. Indeed, the solution to the oxygen equation is identical to the form of the solution obtained by Wyrski (1962) by assuming that respiration is a simple exponential function of depth.

ANALYSIS OF SOLUTIONS: THE GLACIAL OCEAN

The simplest way to view the foregoing equations is in terms of their vertical averages:

$$\overline{PO_4} = PO_{4s} + (\overline{PO_4} - PO_{4s}) \quad (12)$$

$$\overline{O_2} = O_{2s} - r_{O_2:PO_4} (\overline{PO_4} - PO_{4s}) \quad (13)$$

$$\overline{ALK} = ALK_s + 2 r_{Ca:PO_4} (\overline{PO_4} - PO_{4s}) \quad (14)$$

$$\overline{ECO_2} = ECO_{2s} + r_{C:PO_4} (\overline{PO_4} - PO_{4s}) \quad (15)$$

$$\overline{\delta^{13}C} = \delta^{13}C_s + \Delta^{13}C_{PHOTO} r_{Corg:PO_4} \left[\frac{\overline{PO_4} - PO_{4s}}{\overline{ECO_2}} \right] \quad (16)$$

The equations for alkalinity, total carbon, and $\delta^{13}C$ are included for purposes of the discussion below. They are obtained as explained for oxygen and phosphate. The constant " $1/a$ " is larger for $CaCO_3$ than for nutrients, but this drops out in the averaging process. The only alkalinity variations which are considered are those due to removal or addition of $CaCO_3$.

Consider the oxygen equation. This shows that the mean oceanic oxygen levels are determined by the surface oxygen level, the Redfield ratio of oxygen to phosphate, the total phosphate, and the preformed phosphate, PO_{4s} . The first column of Table 1 shows that the mean oxygen level of the oceans and the estimated "preformed" oxygen require quite a high preformed phosphate level. A lower level of preformed phosphate would result in less oxygen in the deep ocean.

A similar sensitivity to the preformed nutrient level is seen with the total carbon and alkalinity. This suggests that one might be able to control the level of atmospheric CO_2 by adjusting the level of preformed nutrients. The second column of Table 1 gives the results of a calculation in which the atmospheric CO_2 was assumed to be 110 ppm lower during the glacial period. This would probably be considered to be an upper limit (e.g., Neftel et al., 1982).

The following equation was used in conjunction with equations (14) and (15) to estimate the change in preformed phosphate required to give the appropriate change in atmospheric CO₂:

$$\frac{\Delta p\text{CO}_2}{(p\text{CO}_2^{\text{IG}} - \frac{\Delta p\text{CO}_2}{2})} = \frac{4\Delta\text{ECO}_{2\text{S}} - 2\Delta\text{ALK}_s}{\left[2(\text{ECO}_{2\text{S}}^{\text{IG}} - \frac{\Delta\text{ECO}_{2\text{S}}}{2}) - (\text{ALK}_s^{\text{IG}} - \frac{\Delta\text{ALK}_s}{2})\right]} + \frac{\Delta\text{ECO}_{2\text{S}} - \Delta\text{ALK}_s}{\left[(\text{ALK}_s^{\text{IG}} + \frac{\Delta\text{ALK}_s}{2}) - (\text{ECO}_{2\text{S}}^{\text{IG}} + \frac{\Delta\text{ECO}_{2\text{S}}}{2})\right]} \quad (17)$$

The mean oxygen level and preformed phosphate are predicted to be dramatically lower during the glacial period. The differences between interglacial and glacial periods for $\delta^{13}\text{C}_s$ and $\delta^{13}\text{C}$ are -0.1 and +0.7, respectively, if we assume a change in the mean ocean $\delta^{13}\text{C}$ of 0.7 due to uptake of carbon by plants and soils, as proposed by Shackleton (1977). The results agree reasonably well with estimates by Broecker (1982) of +0.1 and +0.7 for $\Delta\delta^{13}\text{C}_s$ and $\Delta\delta^{13}\text{C}$ (interglacial-glacial), respectively, from measurements on foraminifera in cores. Our surface $\delta^{13}\text{C}$ can be brought into agreement with the core estimates by increasing the glacial atmospheric CO₂ level by approximately 20 ppm to 220 ppm.

Table 1. Model results for present ocean and an ice age scenario

| | Present Ocean (1) | Glacial Ocean (2) | Difference (interglacial-glacial) |
|---|--|--------------------------|--------------------------------------|
| pCO ₂ (ppm) | 310* | 200* | 110 |
| O _{2s} (μmol kg ⁻¹) | ~300* | ~300* | 0 |
| $\overline{\text{O}_2}$ (μmol kg ⁻¹) | 168* | 50 ^(a) | 118 |
| PO _{4s} (μmol kg ⁻¹) | 1.1 ^(a) | 0.3 ^(e) | 0.8 |
| $\overline{\text{PO}_4}$ (μmol kg ⁻¹) | 2.2* | 2.3 [†] | -0.1 |
| $\delta^{13}\text{C}_s - \delta^{13}\text{C}_{\text{IG}}$ (‰) | 1 ^(b) | 1.8 (1.1)‡ | -0.8 (-0.1) |
| $\delta^{13}\text{C} - \delta^{13}\text{C}_{\text{IG}}$ (‰) | 0* | 0.0 [†] (-0.7)‡ | 0 (0.7) |
| ALK _s (μeq kg ⁻¹) | 2308 ^c | 2344 ^c | -36 |
| $\overline{\text{ALK}}$ (μeq kg ⁻¹) | 2365* | 2488 [†] | -83 |
| ECO _{2s} (μmol kg ⁻¹) | 2106 ^d | 2067 ^d | 39 |
| $\overline{\text{ECO}_2}$ (μmol kg ⁻¹) | 2250* | 2329 [†] | -79 |
| $r_{\text{O}_2:\text{PO}_4} = 120$ | $r_{\text{Corg}:\text{PO}_4} = 105$ | | |
| $r_{\text{Ca}:\text{PO}_4} = 26$ | $\Delta^{13}\text{C}_{\text{PHOTD}} = -20\%$ | | |
| $r_{\Sigma\text{C}:\text{PO}_4} = 131$ | | | |

See Table 2 for footnotes

Broecker (1982) proposes that the increase in atmospheric CO₂ from glacial to present is accompanied by a decrease in ECO₂ and ALK by 6% due to a loss of carbon and CaCO₃ to the sediments. He uses the observed interglacial to glacial changes in δ¹³C_s and δ¹³C discussed above to estimate the change in PO₄ that must accompany the carbon addition. Table 2 gives various concentrations required by his scenario using our model.

Table 2. Model results for present ocean and an ice age scenario based on Broecker's study

| | Present Ocean (IG) (1) | Glacial Ocean (G) | | | |
|---|---------------------------|---------------------------|---------------|--|------|
| | | Our scenario (2) | | Broecker's scenario (3) | |
| | | ΔIG-G | | ΔIG-G | |
| PCO ₂ (ppm) | 310* | 241## | 69 | 241(f) | 69 |
| O _{2s} (μmol kg ⁻¹) | ~300* | ~300* | 0 | ~300* | 0 |
| $\overline{O_2}$ (μmol kg ⁻¹) | 168* | 100(a) | 68 | 62(a) | 106 |
| PO _{4s} (μmol kg ⁻¹) | 1.1(a) | 0.7(e) | 0.4 | PO ₄ -PO _{4s} = 1.9(b)++ | |
| $\overline{PO_4}$ (μmol kg ⁻¹) | 2.2* | 2.3 [†] | -0.1 | | |
| δ ¹³ C _s -δ ¹³ C _{IG} (‰) | 1(b) | 1.4(b) (0.7)‡ | -0.4 (0.3) | 0.9** | 0.1* |
| $\overline{\delta^{13}C}-\overline{\delta^{13}C}_{IG}$ (‰) | 0* | 0 [†] (-0.7)‡ | 0 (0.7) | -0.7** | 0.7* |
| τ (yr) | | 1000 | | 5000 | |
| ALK _s (μeq kg ⁻¹) | 2308 ^c | 2365(c) | -57 | 2480(c) | -172 |
| \overline{ALK} (μeq kg ⁻¹) | 2365* | 2448 [†] | -83 | 2579# | -214 |
| ECO _{2s} (μmol kg ⁻¹) | 2106 ^d | 2119(d) | -13 | 2203(d) | -97 |
| $\overline{ECO_2}$ (μmol kg ⁻¹) | 2250* | 2329 [†] | -79 | 2452# | -202 |

* Estimated from observations (Broecker, 1982; Levitus, 1982).

† Column (1) x 1.035 to correct for decrease in ocean volume.

‡ Values in parentheses include a correction of -0.7% based on benthic foram observations.

** From ΔIG-G observation and column (1).

Column (1) x 1.095 to correct for decrease in ocean volume (3.5%) and increase in ECO₂ and ALK (6%) (Broecker, 1982).

Taken from column (3).

++ Our model allows us only to define the value shown. Broecker uses PO₄ = 3.2 μmol kg⁻¹.

(a) Equation (13)

(b) Equation (16)

(c) Equation (14)

(d) Equation (15)

(e) Equations (14), (15) and (17)

(f) Equation (17)

It also gives results we obtain with our scenario using the glacial atmospheric CO₂ level predicted by Broecker's scenario with our model. A difference between his scenario and ours that is most critical in determining which is more likely to have occurred is the response time. As the ice core measurements become more precise, the data may allow the two scenarios to be differentiated. The disagreement between our ⁸¹³C_s and Broecker's can be removed by our using a glacial atmospheric CO₂ level of approximately 220 ppm, as explained above. Broecker would like the phosphate level to be 3.2 μmol kg⁻¹ in the deep ocean. This is far higher than our model requires, even using Broecker's scenario. The method for estimating phosphate from measurements of cadmium (e.g., Boyle and Kegwin, 1982) should help to identify the phosphate concentrations for the glacial period.

Recent studies have shown that Broecker's scenario of a massive shift of phosphate did not occur, but that there was a massive shift of ECO₂ and thus ALK. The shifts of ECO₂ and ALK are not included in the present study, but are included in the subsequent studies mentioned in the Introduction.

CONCLUSIONS

A change in the ocean circulation and ventilation patterns during the glacial period may have led to a decreased level of preformed phosphate, and this may explain all or part of the change in atmospheric CO₂ concentrations. This scenario has the advantage of not requiring a massive shift of carbon and nutrients from the shelves to the oceans. It should be possible to decide between the two scenarios by looking at the record of cadmium in foraminifera as an indicator of deep ocean phosphate levels, as well as looking at the time scale of change in CO₂.

It hardly need be pointed out that a shift in preformed nutrient levels could also have a significant impact on the ocean's capacity to take up fossil fuel CO₂, though the time scale of such shifts may be too long to have a significant impact on a decadal time scale. It is extremely important for us to gain a deeper understanding of how the level of preformed nutrients in the oceans is determined and how this can change. An improved understanding of upper ocean chemical dynamics, particularly in deep water formation areas, is crucial.

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