

CAUSES OF ANOXIA IN THE WORLD OCEAN

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Abstract. We examine the hypothesis that global scale episodes of anoxia such as occurred in the Cretaceous are due to high productivity and/or stagnation of the circulation. Two modes of ocean circulation are considered: a thermohaline overturning cell, essentially vertical, which involves global scale upwelling into the surface followed by sinking in deep water formation regions; and an approximately horizontal cell which connects the abyss directly with deeply convecting waters in deep water formation regions. Modern analogs for these processes are formation of North Atlantic Deep Water and Antarctic Bottom Water, respectively. Over most of the oceans the surface new production is nutrient limited and thus directly proportional to the supply of nutrients by the vertical overturning cell. A reduction in oxygen can only be brought about by increased vertical overturning associated with increased production. In addition, the model shows that as the deep ocean becomes lower in oxygen, the sensitivity of the oxygen levels to the meridional circulation decreases such that it becomes difficult or impossible to achieve

complete anoxia. This relative insensitivity of deep ocean oxygen levels to the magnitude of the vertical overturning cell and associated surface production may explain why it has been difficult to establish a clear connection between high surface productivities in low and mid-latitudes and anoxia. In deep water formation regions, on the other hand, new production is not nutrient limited. A reduction in abyssal oxygen can be brought about by high productivity in such regions and/or by stagnation of the horizontal circulation cell, in accordance with the stagnation hypothesis. Furthermore, the sensitivity of the deep ocean oxygen to the processes occurring in deep water formation regions increases as oxygen levels decrease. We therefore suggest that processes occurring in deep water formation regions may be the critical ones in determining deep ocean oxygen.

INTRODUCTION

There exists considerable evidence through time of widespread episodes of anoxia in the oceans [Schlanger and Jenkyns, 1976; Ryan and Cita, 1977; Arthur et al., 1984]. These episodes have usually been interpreted as arising from generalized increases in surface productivity and/or stagnation of ocean circulation. However, the relationships between the productivity and circulation

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on the one hand, and the oceanic distributions of oxygen, carbon, and nutrients on the other, has not, on the whole, been explored quantitatively with only a few exceptions [e.g., Southam et al., 1982; Wilde and Berry, 1982; Bralower and Thierstein, 1984]. Our study of the chemistry of the ice age ocean [Sarmiento and Toggweiler, 1984; Toggweiler and Sarmiento, 1985] has led us to conclude that the relationships between surface biological productivity, the rate of ocean circulation, and the oxygen level of the deep waters are different in many respects from the simple conceptual and quantitative models that have guided most previous studies. We demonstrate here how the mass balance modeling approach we have used in our earlier studies of the ice age ocean can also give insight to processes that might have occurred during the Cretaceous.

The purpose of this paper is to present a set of simple nutrient and oxygen balance models from which one can obtain quantitative estimates of the conditions that are necessary for the development of anoxia in "closed" basins such as the world ocean. By anoxia, we mean levels of oxygen low enough that benthic organisms are unable to survive and sediments become laminated. The most unambiguous evidence for anoxia in the geologic record is lamination and the absence of benthic fossils. High organic carbon contents, which are often taken to indicate the presence of anoxia, may result from high productivities even when oxygen is present. A separate paper considers the oxygen balance in "open" basins such as the Mediterranean [J.L. Sarmiento et al., Mediterranean nutrient balance and episodes of anoxia, submitted to Global Biogeochemical Cycles, 1988; hereinafter Sarmiento et al. 2).

The observed time scale of anoxic episodes in the past provides an important clue to the components which must be included to provide a first-order description of the dynamics of oxygen depletion in the Mesozoic to Recent ocean. Previous studies [Weissert et al., 1979; Dean et al.; 1978, Arthur et al., 1984; Herbert and Fischer, 1986] have shown that the duration of anoxia in various ocean basins was typically a few kiloyears to tens of kiloyears, with rapid transitions of the order of a few kiloyears. Sediments that accumulated under conditions of low dissolved oxygen

are interbedded with bioturbated, normally oxygenated deposits. Thus individual anoxic events were too short to involve long-term controls on climate and ocean circulation such as continental drift and the tectonic CO₂ cycle which have been explored by Berner et al. [1983]. The mean oceanic PO₄ cycle, presuming a residence time approximately equal to the modern value of the order of 100,000 years [Froelich et al., 1982], can also be neglected. Nitrate, with its estimated residence time of order 10,000 years [McElroy, 1983] may play a more complex role in limiting the cycling of oxygen, as discussed by Knox and McElroy [1984], because of its shorter residence time and the fact that its removal rate from the oceans by denitrification is sensitive to the oxygen content. However, its residence time in the modern ocean seems too long to explain the rapid transitions from anoxia to oxygenation. While long-term climate change may broadly determine susceptibility of an ocean basin to anoxia, we look for internal features of the ocean-climate system which could mediate the transition between oxygenated and anoxic deep waters quite rapidly.

We derive a model for a closed basin, i.e., one with no substantial exchange with other basins, considering the present and Cretaceous oceans as examples. Such a model would be representative of the world ocean as well as of smaller enclosed basins. We show here the dominant importance of processes occurring in local regions of deep water formation. It is possible in principle to obtain anoxia with either high or low global scale surface productivities coupled with rapid or slow "upwelling", respectively, as long as the appropriate set of conditions is met in the local regions where deep waters are forming. It is this independence of the global scale productivity from the deep ocean oxygen levels that marks our model as different from previous conceptual models.

We should point out that the models we use are very simple box models that do not show how the vertical profile of oxygen will vary under different conditions. Appropriate models, such as those of Boyle [1986] and Knox and McElroy [1984], both of whom include a single thermocline box, or the more highly resolved model of Southam et al. [1982], are not difficult to construct; but their interpretation is more complex than that of the simple

models we use here. One of the major features of our models is the direct linkage between low-latitude upwelling and deep water formation through large-scale thermohaline overturning. In models with greater vertical resolution, this linkage is not as direct as in our model. The effect of this difference will be discussed later in the paper.

CRETACEOUS ANOXIC EVENTS

Cores raised by the Deep Sea Drilling Project (DSDP) suggest that periodic anoxia, identified by finely laminated sediments, was a common feature of the lower Cretaceous (125-90 m.y B.P.) ocean (see reviews by Weissert [1981] and Arthur et al. [1984]). Because the duration of individual anoxic events was brief it is difficult to determine the degree of synchronicity of oxygen depletion in different basins, and even within basins (see Waples [1983] for a skeptical view). However, at least in the case of the Cenomanian-Turonian boundary event, the anoxic realm demonstrably included the entire North Atlantic Basin, the Tethyan Basin, the U.S. Western Interior Basin, and portions of the Pacific and Indian Oceans [de Graciansky et al., 1984; Schlanger et al., 1987]. Clues to the origin of deep water Cretaceous organic carbon enriched deposits have been sought by sedimentological [McCave, 1979; Arthur, 1979; Dean et al., 1978], inorganic and organic geochemical [Dean et al., 1984; Herbert and Fischer, 1986; Tissot et al., 1979; Summerhayes, 1981; Meyers et al., 1984], carbon isotopic [Dean et al., 1986], and oceanic modeling [Southam et al., 1982; Wilde and Berry, 1982; Bralower and Thierstein, 1984] studies.

The investigations of one of us (T.H.) have focused on the timing of transitions from bioturbated intervals to laminated black zones in an Aptian-Albian core from central Italy [Herbert and Fischer, 1986; Herbert et al., 1986]. These sediments were deposited in a water depth of a few kilometers [Arthur and Premoli Silva, 1982] in the west-east running Tethyan Ocean which connected the Atlantic and Pacific Oceans. The laminated beds are clearly not turbiditic in origin, and display the following vertical sequence: a zone of organic-rich burrows in a green matrix grades upward into a solidly black, but unlaminated zone and finally becomes minutely laminated. We interpret this

sequence to represent progressive deoxygenation of deep water O₂ content of the Tethyan Basin.

Anoxic deposits make up about 5% of the thickness sampled for time series analysis. Black shales fall within a hierarchy of geochemical oscillations in which harmonic components matching the earth's orbital eccentricity, obliquity, and precessional cycles can be recognized [Park and Herbert, 1987; T. Herbert and J. Park, unpublished manuscript, 1987]. Individual episodes of anoxia occur as peaks of an approximately 20-kyr (precessional) cycle, in a pattern similar to that observed in DSDP cores [Dean et al., 1978, 1984; McCave, 1979; Arthur, 1979]. We infer that the climate rhythms caused basin-wide variations in oxygenation on this time scale.

Geochemical sampling of the Italian sequence reveals a consistent pattern: by assuming that the orbital cycles act as an internal clock to monitor sedimentation rate, it can be shown that the concentration of biogenic components (carbonate and silica) is always higher in oxygenated intervals than in anoxic beds (see Figure 1; Herbert et al. [1986]). The magnitude of the cycles is large: carbonate and silica accumulation vary by a factor of 1.5-2 over 20 kyr, by 3-4 over 100 kyr, and by 4-5 over 400 kyr. As there is no evidence that differential dissolution controls the biogenic content of these sediments, the accumulation patterns of carbonate and silica appear to trace an orbital-climatic modulation of the rate of upwelling of nutrient-rich deep water, which leads to high productivity and limestone accumulation at the time when oxygen levels are high, and low productivity and black shale deposition at times when anoxia prevails.

Anoxic zones are very restricted in the modern ocean. Therefore, the widespread occurrence of low oxygen deposits in the mid-Cretaceous may imply fundamental changes in oceanic circulation and/or the rate and mode of delivery of organic matter to the deep sea. Debate as to the mode of formation of deep water Cretaceous black shales has split primarily along three lines: a stagnation model with several subvariants [Fischer and Arthur, 1977; Ryan and Cita, 1977; Thierstein and Berger, 1978; Arthur and Schlanger, 1979; de Graciansky et al., 1984], increased carbon supply models [Dean et al., 1978; Jenkyns, 1980; Habib,

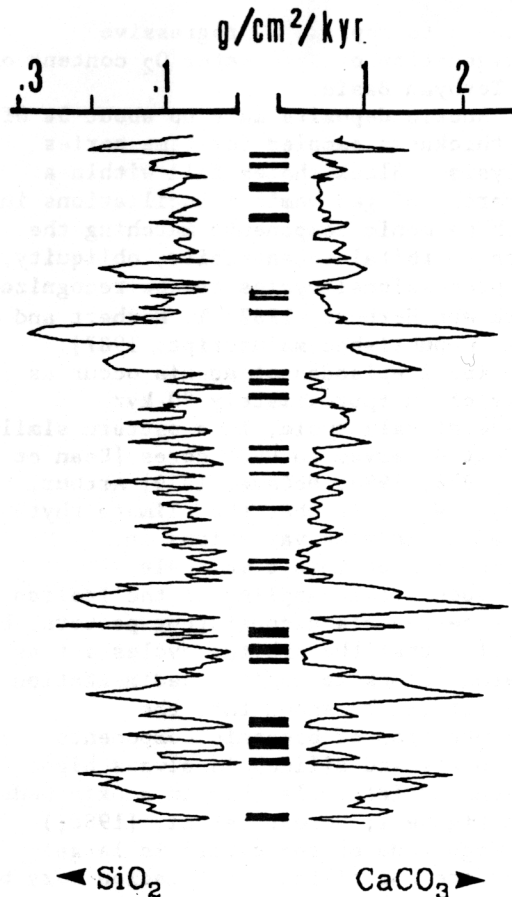


Fig. 1. Fluxes of carbonate and biogenic silica, upper Albian of Piobbico core, in relation to occurrences of anoxic bands, shown as solid intervals. Weight percent data are converted to fluxes by normalizing to aluminum, which accumulated at a nearly constant rate [see Herbert et al., 1986].

1982], and the warm saline bottom water hypothesis [Brass et al., 1982].

Proponents of the stagnation model argue that slow renewal of deep water during the Cretaceous was the key factor in promoting anoxia. The oxygen minimum concept [Fischer and Arthur, 1977] suggests that Cretaceous waters were chronically poorly oxygenated because of sluggish circulation and warmer deep water temperatures. Organic carbon rich beds would then form in the deep sea from periodic expansion of an intense midwater O_2 minimum zone through an unspecified mechanism. This idea would predict that sites which were at mid-depth (0.5-1.5 km paleodepth) during the mid-Cretaceous

should show the most intense development of anoxia. While this is true for some basins (Pacific), in many cases anoxia seems to have developed to an equal or greater extent in deeper waters [Weissert et al., 1979; Tucholke and Vogt, 1979; Waples, 1983]. In any event there appear to be few areas which remained continuously anoxic; nearly all black shale sequences consist of a minority of black bands intercalated with dominantly bioturbated, drab to red sediments indicative of oxygenated bottom water [Dean et al., 1978; Hay et al., 1982; Arthur et al., 1984].

In the stratified basin model of stagnation [Ryan and Cita, 1977; Thierstein and Berger, 1978], the locus of anoxia is in basinal areas, which are hypothesized to have received very little renewal of oxygen because of strong vertical density gradients. This is essentially the "open" basin case that is discussed in Sarmiento et al. 2. In that paper we show that anoxia in such basins is linked to the supply of nutrients to the basin, and not to the rate of circulation. In any case, the large size of the North Atlantic, even during the mid-Cretaceous, makes analogies to modern salinity-stratified basins (for example, Black Sea, Cariaco Trench) seem tenuous [e.g., Dean and Gardner, 1982].

Dean and Gardner [1982] have proposed that bottom waters need not have been anoxic at all. Instead, they argue that periodic rapid supply of organic matter is involved, either by high productivity, or turbidity current deposition, as a means of deoxygenating sediment pore water and possibly a thin layer above the sediment-water interface [Dean et al., 1978; Dean and Gardner, 1982; Habib, 1982]. The results of T. Herbert and J. Park [1987], discussed above, do not support this picture, in that anoxia is associated with a lower rather than higher supply of carbonate and silica. The low organic carbon contents in the limestones of the Italian sequence are interpreted to result from rapid degradation in the highly biogenic beds due to the well-oxygenated environment.

The warm saline bottom water hypothesis of Brass and colleagues provides a mechanism for generally decreased oxygen levels, but not for rapid changes in these levels. Wilde and Berry [1982] provide a mechanism for changes in the oxygen which involves shifts from warm

deep water formation to cold deep water formation. Our model incorporates within it the potential for processes such as those suggested by these authors.

Time series observations suggest that the Tethyan ocean basin, far from being sluggish, as is usually assumed for the mid-Cretaceous [Fischer and Arthur, 1977; Bralower and Thierstein, 1984], resembled the modern ocean surprisingly closely in its sensitivity to orbital forcing. The model developed below is attractive for several reasons: it is capable of generating large rapid changes in deep sea oxygenation by changes in internal parameters only; it is flexible in that varying degrees of deoxygenation can occur under different combinations of parameters; and it includes features such as thermohaline circulation and deep water formation characteristics that are likely to be controlled by Milankovitch-style climate oscillations.

CLOSED BASIN MODEL

The key to our model is the importance of deep water formation processes in determining deep ocean oxygen levels. This can be best illustrated, as in Sarmiento [1986], by a model that does not work for oxygen for the present ocean: a two-box model such as the one Broecker and Peng [1982] use to study a variety of other chemicals. Consider the simplified version of this model shown in Figure 2, where f represents the exchange between the surface and deep box and P is the particulate rain in phosphate units from the surface. River input and loss to sediments affect large scale nutrient distributions on the time scale of the oceanic residence time of the nutrient of interest. These changes occur too slowly to be of interest to us and these processes are therefore assumed to have a negligible effect on the interior distribution of properties that we are interested in. The practical consequence of this assumption is that all of the particulate rain to the deep sea is returned to solution. One can obtain a simple steady state solution for this model by using the deep box phosphate balance:

$$P = f(\text{PO}_4\text{d} - \text{PO}_4\text{s}) \quad (1)$$

and the deep box oxygen balance:

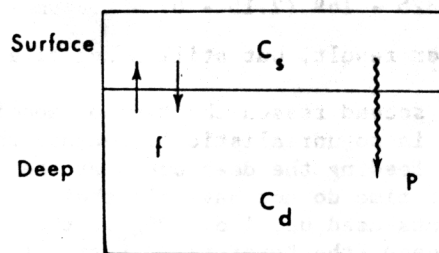


Fig. 2. A two-box model of the oceans. Here f represents the exchange between the surface and deep box and P is the particulate rain of phosphate.

$$rP = f(O_2\text{s} - O_2\text{d}) \quad (2)$$

where r is the Redfield ratio of oxygen consumption to PO_4 production accompanying the oxidation of organic matter. Substituting (1) into (2) and solving for $O_2\text{d}$ gives

$$O_2\text{d} = O_2\text{s} - r(\text{PO}_4\text{d} - \text{PO}_4\text{s}) \quad (3)$$

We could as easily solve the same problem by using ΣCO_2 or any other organically cycled substance in place of PO_4 . The advantage of using PO_4 is that it is from a geochemist's point of view the limiting nutrient inasmuch as there is always plenty of carbon, and NO_3 is produced as well as consumed by organisms such that it is possible for them to redress imbalances that may occur, given enough time [Broecker and Peng, 1982, p. 284].

We now see if (3) can predict the present ocean. $O_2\text{s}$ has a global average of $\sim 240 \mu\text{mol/kg}$, r is ~ 169 [Takahashi et al., 1985], $\text{PO}_4\text{d} \sim 2.15 \mu\text{mol/kg}$, and PO_4s averages approximately zero in low and middle latitudes of the world ocean. This gives

$$O_2\text{d} \sim 240 - 169(2.15 - 0) = -123 \mu\text{mol/kg}$$

compared with an observed value of $\sim 168 \mu\text{mol/kg}$. Why does the model give such unrealistic results? There are two reasons. The first is that the waters feeding the deep ocean at the present time are cold and have higher oxygen than the world average surface oxygen. If we use a more realistic value for the $O_2\text{s}$ feeding the deep ocean of $\sim 325 \mu\text{mol/kg}$ we predict for the deep ocean oxygen a value of

$$O_{2d} = 325 - 169 (2.15 - 0) = -38 \mu\text{mol/kg}$$

a better result, but still a negative one.

The second reason the two-box model result is so unrealistic is because the waters feeding the deep ocean at the present time do not have all their nutrients used up, i.e., PO_4 in the deep ocean (the "preformed" nutrient content) is not zero. These waters are therefore supplying high oxygen without introducing the oxygen demand that would be required if all the nutrients that came in contact with the surface were utilized by organisms and sent down to the abyss in the reduced particulate form. We show below that the observed O_{2d} of $\sim 170 \mu\text{mol/kg}$ can be obtained with a model including high-latitude deep water formation by using a value of $\sim 1.2 \mu\text{mol/kg}$ for the PO_4 content of the high-latitude waters:

$$O_{2d} = 325 - 169 (2.15 - 1.24) = 170 \mu\text{mol/kg}$$

Note that it is conceivable that an ocean behaving like the above two-box model and governed by (3) could exist. Such an ocean would have deep water forming predominantly in low latitudes with extremely low preformed nutrient values (PO_4). In order to get any oscillations in the deep ocean oxygen level, the deep ocean phosphate level, PO_{4d} , would have to oscillate as well. Changes in deep ocean PO_4 have been postulated by Broecker [1982] based essentially on a two-box model such as the above to explain the ice age decrease in atmospheric CO_2 . This is also essentially how Southam et al. [1982] obtain anoxia in their model. They do not explicitly acknowledge this in their paper, but it can be inferred from their use of the Wrytki [1962] approach and from the further description of their model in Southam and Peterson [1985]. However, as pointed out in the introduction, the time scale for changes in the total phosphate content of the oceans is governed by sources and sinks at the ocean boundaries, not by processes internal to the ocean, and is of the order of 100,000 years.

Given the importance of the high-latitude processes it makes sense to go the next step in model complexity by introducing a high latitude surface box to the model as shown in Figure 3. This is the same model that has been used by

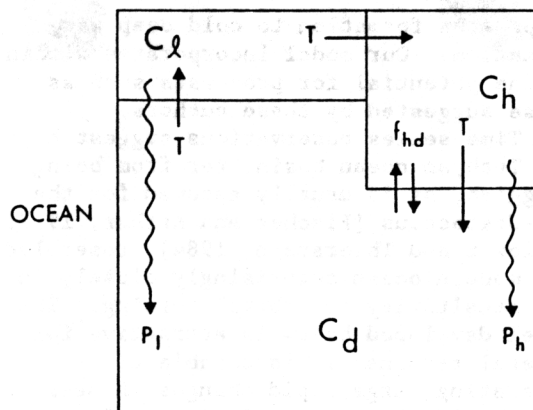


Fig. 3. A three-box model of the oceans. The subscripts l , h , and d stand for low-latitude surface, high-latitude surface, and deep ocean, respectively. The high-latitude ocean represents the regions where deep water is forming, which are very small in area compared with the remainder of the surface ocean represented by the l box. T and f_{hd} are circulation parameters. T is analogous to the large-scale thermohaline overturning represented in the present ocean by formation of North Atlantic deep water. The major characteristic of T is the fact that it upwells and circulates through the l box. Toggweiler and Sarmiento [1985] obtain a value of $19 \times 10^6 \text{ m}^3\text{s}^{-1}$ for T in the present ocean. The parameter f_{hd} , with a present value of 45 to $60 \times 10^6 \text{ m}^3\text{s}^{-1}$, represents local convective overturning in deep water formation regions which is analogous in the present ocean to formation of Antarctic bottom water. P is the particulate rain of phosphate from the high-latitude deep water formation region (P_h) and low-latitude surface ocean (P_l).

numerous investigators to study the ice age ocean [Sarmiento and Toggweiler, 1984; Knox and McElroy, 1984; Siegenthaler and Wenk, 1984; Ennever and McElroy, 1985; Toggweiler and Sarmiento, 1985; Wenk and Siegenthaler, 1985]. Toggweiler and Sarmiento [1985] have made an effort to relate the physical exchange processes, f_{hd} and T , in the model to the processes observed in the present ocean. They make the case that the f_{hd} term is essentially a strong convective overturning involving primarily deep water brought up to the surface, cooled, oxygenated and then returned to the abyss, much like what

occurs around the Antarctic. T is a large-scale thermohaline overturning term involving the transport of low-latitude surface waters to high latitudes and the cooling and sinking of these waters. This is similar to what occurs in the North Atlantic with the formation of North Atlantic deep water (NADW).

A simple steady state solution for the deep ocean oxygen in this model can be obtained as above in the two-box model case by solving first for the particle fluxes, P_l and P_h , in this case from surface box PO_4 balances; and by assuming for simplicity that all the PO_4 entering the low-latitude surface ocean is utilized ($PO_{4l} - 0$), which is approximately in agreement with present observations:

$$P_l = PO_{4d} \cdot T \quad (4)$$

$$P_h = PO_{4d} \cdot f_{hd} - PO_{4h} \cdot (f_{hd} + T) \quad (5)$$

The subscripts "l" and "h" refer to the low- and high-latitude surface boxes, respectively. Substituting (4) and (5) into the deep ocean oxygen balance equation:

$$r (P_l + P_h) = O_{2h} (f_{hd} + T) - O_{2d} (f_{hd} + T) \quad (6)$$

and solving for O_{2d} , gives

$$O_{2d} = O_{2h} - r (PO_{4d} - PO_{4h}) \quad (7)$$

Equation (7) is able to predict the present oxygen values with a PO_{4h} value of 1.24 $\mu\text{mol/kg}$:

$$O_{2d} = 325 - 169 (2.15 - 1.24) = 170 \mu\text{mol/kg}$$

The value of 1.24 $\mu\text{mol/kg}$ for PO_{4h} is quite reasonable given what we know about the high-latitude deep water formation regions.

We are now ready to address the question of how the deep ocean oxygen can change through time. Equation (7) tells us that the deep ocean oxygen content is a function first of the oxygen content of the waters feeding the deep ocean, O_{2h} . O_{2h} depends primarily on the temperature dependent solubility of oxygen. For example, if deep water formation were to shift from high to low latitudes, the

oxygen solubility and therefore O_{2h} might drop by as much as 85 $\mu\text{mol/kg}$ from ~325 $\mu\text{mol/kg}$ to ~240 $\mu\text{mol/kg}$. This would be enough in and of itself to lead to anoxia in large areas of the present Pacific. However, although there is evidence that deep ocean temperatures were warmer (10-15°C warmer) during the Cretaceous than at present [Savin, 1977; Brass et al., 1982], there is as yet no clear evidence we are aware of for the short-term changes in this temperature which would be required to explain the cycling in and out of anoxia which is observed. We therefore assume that changes in O_{2h} are not a major contributing factor in anoxic events. Another interesting consideration is that atmospheric oxygen levels may have been different in the Cretaceous than at present. This would change the baseline for our calculations and might alter the sensitivities somewhat, but it would not alter the basic arguments as to what causes the variability.

The remainder of (7) tells us that O_{2d} is a function of the Redfield ratio of oxygen to phosphate, r , and of the difference between deep ocean phosphate, PO_{4d} , and preformed phosphate, PO_{4h} . We have no way of estimating how the Redfield ratio may have changed through time nor any basis for speculating how it may have changed rapidly enough to explain the observed oxygen cycles. We therefore confine our attention to the phosphate. We presume that variations in the average oceanic phosphate are part of the preconditions for anoxia to occur. The ambient level of phosphate is determined in part by the river input of phosphate, which is what fixes the amount of phosphate that must be buried in the sediments [Broecker, 1971]. The higher the river flux, the higher the average oceanic phosphate, and vice versa. As discussed above, however, variations in average oceanic phosphate due to processes such as these occur over a long time scale and cannot explain the short time scale variations we are interested in.

This leaves us, finally, with the high-latitude phosphate, PO_{4h} , as the key parameter in (7). The deep ocean oxygen varies in direct proportion to it; the larger PO_{4h} is, the larger O_{2d} , and vice versa. For the present ocean to go anoxic, PO_{4h} would have to drop from its present value of ~1.24 $\mu\text{mol/kg}$ to a value

of $-0.23 \mu\text{mol/kg}$. The residence time of water in the surface high-latitude oceans (~ 5 to 7 years at present in the Toggweiler and Sarmiento [1985] model) is quite short, which means that $\text{PO}_{4\text{h}}$ can change very rapidly. Once $\text{PO}_{4\text{h}}$ changes, the deep ocean oxygen will adjust on the time scale of the residence time of water in the deep ocean, which is presently ~ 1000 years. So our problem is now reduced to asking what climate sensitive parameters control $\text{PO}_{4\text{h}}$.

It is useful at this point to return to a consideration of the three independent equations, (4), (5), and (6), from which (7) was derived. These equations have nine "unknowns": P_l and P_h , f_{hd} and T , $\text{PO}_{4\text{h}}$ and $\text{PO}_{4\text{d}}$, $\text{O}_{2\text{h}}$ and $\text{O}_{2\text{d}}$, and r . We have given arguments above for assuming that three of these unknowns, $\text{PO}_{4\text{d}}$, $\text{O}_{2\text{h}}$, and r , do not change significantly on the time scale of the oxygen cycling. If we treat these three parameters as "knowns," we are left with six unknowns. Two of the equations are used to obtain solutions for $\text{PO}_{4\text{h}}$ and $\text{O}_{2\text{d}}$, leaving us with four unknowns and one additional equation. Of the remaining four unknowns, P_l , P_h , f_{hd} , and T , only three might be expected to vary directly with climate and, at least in principle, independently of each other: the circulation parameters, f_{hd} and T , and the high-latitude particle production rate, P_h . P_h is not limited by nutrient supply at present, as is P_l , but rather by a poorly understood combination of factors such as light availability, mixed layer thickness, and ice formation, many of which would be expected to be sensitive to changes in climate and/or the distribution of light falling on the Earth. The third equation is therefore used to eliminate P_l , whose magnitude is limited by the nutrients supplied by T , not directly by light or climate, and therefore cannot vary independently of T ; and we retain f_{hd} , T and P_h as the independent variables which between them fix the value of $\text{PO}_{4\text{d}}$ and $\text{O}_{2\text{d}}$.

We can obtain a solution for $\text{PO}_{4\text{h}}$ in terms of the three independent variables and the "known" $\text{PO}_{4\text{d}}$ by rearranging (5):

$$\text{PO}_{4\text{h}} = \frac{\text{PO}_{4\text{d}} f_{\text{hd}} - P_h}{f_{\text{hd}} + T} \quad (8)$$

Equation(8) shows that $\text{PO}_{4\text{h}}$ is sensitive to the average deep ocean phosphate, $\text{PO}_{4\text{d}}$, which we have argued does not change rapidly enough to explain the anoxia cycles. The important terms in (8) are therefore the high-latitude export of particulate phosphate, P_h , and the two physical exchange parameters, f_{hd} and T . We can now find the sensitivity of $\text{O}_{2\text{d}}$ to each of these three parameters by making use of the chain rule and (8), and the relationship $\partial \text{O}_{2\text{d}} / \partial \text{PO}_{4\text{h}} = r$. For the effect of high latitude deep water formation,

$$\frac{\partial \text{O}_{2\text{d}}}{\partial f_{\text{hd}}} = \frac{\partial \text{O}_{2\text{d}}}{\partial \text{PO}_{4\text{h}}} \frac{\partial \text{PO}_{4\text{h}}}{\partial f_{\text{hd}}} = r \frac{\text{PO}_{4\text{d}} - \text{PO}_{4\text{h}}}{f_{\text{hd}} + T} \quad (9)$$

for the effect of the large-scale meridional overturning,

$$\frac{\partial \text{O}_{2\text{d}}}{\partial T} = \frac{\partial \text{O}_{2\text{d}}}{\partial \text{PO}_{4\text{h}}} \frac{\partial \text{PO}_{4\text{h}}}{\partial T} = -r \frac{\text{PO}_{4\text{h}}}{f_{\text{hd}} + T} \quad (10)$$

and for the effect of high-latitude productivity,

$$\frac{\partial \text{O}_{2\text{d}}}{\partial P_h} = \frac{\partial \text{O}_{2\text{d}}}{\partial \text{PO}_{4\text{h}}} \frac{\partial \text{PO}_{4\text{h}}}{\partial P_h} = -r \frac{1}{f_{\text{hd}} + T} \quad (11)$$

Equations (9) and (10) have been simplified after differentiation by eliminating P_h with (5).

What conclusions can we draw from the above results? Consider first (9) and (10). We shall show at the end of our discussion that the dependence of $\text{O}_{2\text{d}}$ on P_h (equation (11)) is similar, though of opposite sign, to the dependence of $\text{O}_{2\text{d}}$ on f_{hd} . (This is because, over most of the range we are interested in, $\text{PO}_{4\text{d}} - \text{PO}_{4\text{h}}$ is of order $1 \mu\text{mol kg}^{-1}$.) The right-hand side of (9) is always positive whereas that of (10) is always negative. A first conclusion is therefore that stagnation of the circulation, when it refers to f_{hd} , will lead to lower oxygen levels, in agreement with earlier thinking on the subject. However, T , which is linked directly to low-latitude upwelling and productivity, is inversely related to the

deep ocean oxygen. In order to reduce the oxygen we must increase T and, therefore, increase the low-latitude productivity (see equation (4)). The relationship between oxygen content and circulation and low-latitude productivity is subtle. Stagnation and a global scale increase in productivity (P_l) do lead to lower oxygen contents, but great care needs to be taken in specifying what type of circulation is stagnating; and it needs to be understood that an increased productivity implies an increase in upwelling and in the meridional overturning circulation that is associated with this upwelling.

The picture becomes even more complex when we consider what happens to (9) and (10) as we approach anoxia. We have shown above that PO_{4h} becomes small as we approach anoxia (equation (7)), whereas PO_{4d} remains essentially constant. From (9) and (10) we see that the sensitivity of O_{2d} to f_{hd} increases as PO_{4h} becomes smaller, whereas the sensitivity of O_{2d} to T decreases. A second conclusion, therefore, is that as we approach anoxia due to greater nutrient utilization at high latitudes (lower PO_{4h}), the global scale low-latitude productivity (P_l) and large-scale thermohaline overturning of the type represented by T are able to change over very large ranges without having an appreciable effect on deep ocean oxygen levels. This can also be seen in Figure 4, which shows the deep ocean oxygen as a function of f_{hd} and T with all other parameters at their present values. The reason O_{2d} becomes less sensitive to T is because the oxygen demand introduced by P_l and the supply of oxygen from the high latitude by T come fairly close to balancing each other.

The above arguments apply to an ocean with an average phosphate level similar to that at present. How does the response of the ocean change if the phosphate level changes? An increased phosphate level will increase PO_{4d} . We can see from (7) that this will decrease the deep ocean oxygen unless PO_{4h} also increases so that the difference ($PO_{4d} - PO_{4h}$) remains approximately the same. Returning to (9) and (10) we might therefore conclude that O_{2d} will become more sensitive to T and relatively less sensitive to f_{hd} as the total phosphate increases and vice versa. Solving the full model leads to a more complex situation, but the basic arguments

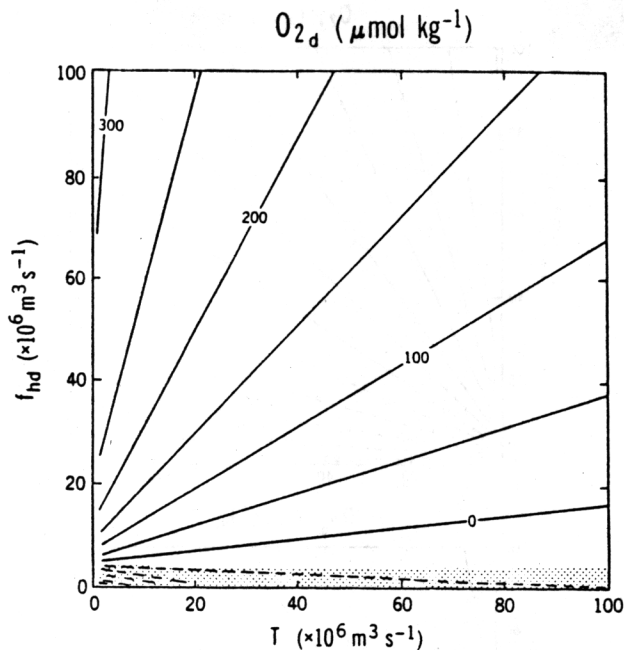


Fig. 4. The deep ocean oxygen predicted by the three box model of Figure 3 using (7) and (8). P_h is taken to be 0.5 moles $C\ m^{-2}yr^{-1}$ [Toggweiler and Sarmiento, 1985]. The main point of this figure is that as the ocean approaches low levels of oxygen it becomes very insensitive to T . Also, note that anoxia is associated with increasing T but with decreasing f_{hd} . Stippling indicates regions where the PO_{4h} predicted by the model is negative. The dashed oxygen contour lines are negative.

apply. In Figure 5 we show how deep ocean oxygen levels respond to f_{hd} and T when the phosphate content of the ocean is raised and lowered by 50% from its modern value. With more phosphate in the ocean the oxygen content of the deep ocean becomes more sensitive to the circulation parameters. With less phosphate, anoxia occurs only with extremely low values of f_{hd} and T . If the phosphate value is increased by 50%, the oxygen content becomes more sensitive to the thermohaline overturning, T , as expected.

Figure 6 shows the sensitivity of oxygen to P_h and T . The similarity of this plot to that of Figure 4 justifies our earlier argument that P_h and f_{hd} behave very similarly. Given the decrease in sensitivity of deep ocean oxygen to T as anoxia is approached, we conclude that episodes of anoxia are due primarily to

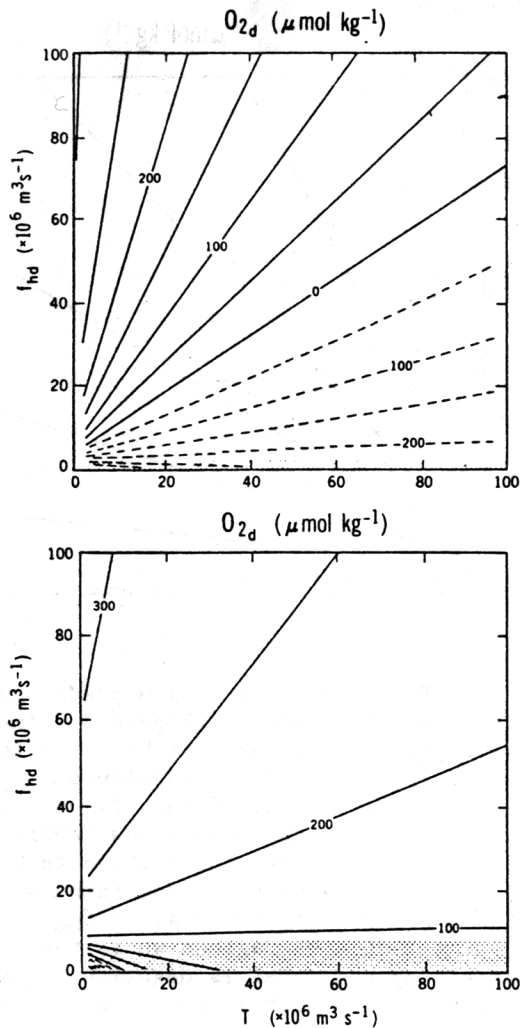


Fig. 5. Same as Fig. 4, except that the upper panel is for a total ocean phosphate 50% higher than the present level used in Fig. 4, and the lower panel is for a 50% lower total phosphate. Note the greatly increased sensitivity to T in the upper panel. The experiment represented by the lower panel has such low total phosphate that there is essentially no anoxia within the parameter range shown. As in Fig. 4, stippling indicates regions where the PO_{4h} predicted by the model is negative and the dashed oxygen contour lines are negative.

changes in P_h and f_{hd} . Notice from (8) that f_{hd} and P_h can counterbalance each other in the sense that an increase in one can be compensated for by an increase in the other, and a decrease in one can be compensated for by a decrease in the

other. Again, as with T and P_h , we see that there is considerable latitude for changes in the magnitude of productivity and the circulation.

DISCUSSION

A key feature of the three-box model is that temperatures and nutrient utilization rates in regions of deep water formation may not be identical to values for mean surface water. What is the evidence for such a three-box ocean in mid-Cretaceous time? The strongest argument is the fact that there were rapid changes in deep ocean oxygen levels. If the deep water formation always occurred with properties identical to mean surface water, then we are back to the two-box model discussed above with all its attendant problems.

We therefore prefer to develop a scenario for mid-Cretaceous anoxic events which includes high-latitude deep water formation. We have seen that a slowing of the large scale thermohaline overturning (T in our model) will not in and of itself induce anoxia. Indeed, from Figures 4, 5, and 6 we can see that a slowing of T will lead to an increase in oxygen. The key to rapid deoxygenation more likely lies in

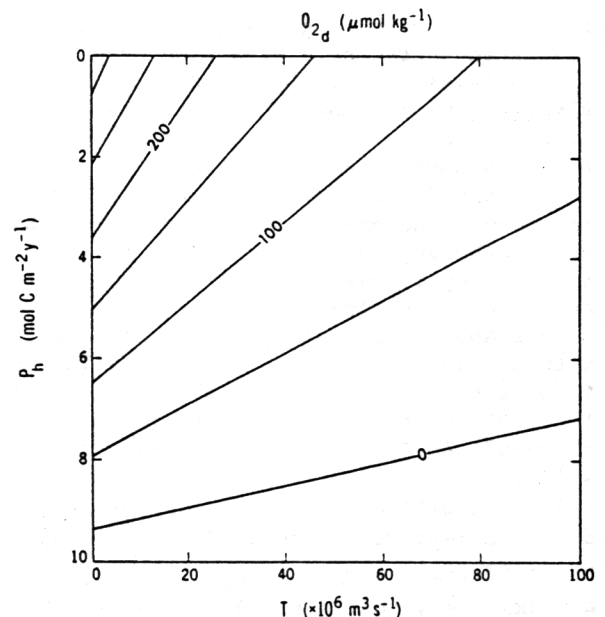


Fig. 6. The deep ocean oxygen as a function of P_h and T . The scale for P_h has been inverted to emphasize the similarity of P_h and f_{hd} (see Fig. 4) in their effect on oxygen. Here f_{hd} is held at a value of $48 \times 10^6 \text{ m}^3 \text{ s}^{-1}$.

modifying the rate and/or chemical characteristics of deep water formation.

Figure 4 shows that deep water O_2 decreases steeply with a decrease in f_{hd} , the rate of formation of deep water. Thus, if the climatic factors which promote a slowing of the meridional circulation (T) act similarly on deep water formation (f_{hd}), the effect would be to produce anoxia under low-productivity conditions. Another potent source of change would be climatic modulation of the fraction of nutrients consumed in the source region of deep water. A shift toward greater consumption of nutrients would promote anoxia, and could plausibly be related to orbital cycles by increased light availability in high latitudes, or a shift in deep water formation [Brass et al., 1982] to lower latitudes where light availability is greater [e.g., Knox and McElroy, 1984].

A scenario of periodic shifts to deep water formation in lower latitudes resembles the "warm saline bottom water" hypothesis of Brass et al. [1982] and Wilde and Berry [1982], with the distinction that in our model a critical effect is the change in nutrient utilization, rather than the decrease in deep water O_2 solubility with increased temperature. The two effects shift deep water O_2 in the same direction. The relative importance of the controls identified in the three-box model compared to temperature changes can be gauged from the preceding discussion on the oxygenation of the modern ocean (the possible range of temperatures in the Cretaceous ocean probably did not exceed 15°).

The three-box model has the advantage over previous ad hoc models of Cretaceous anoxic events in that it can account for a diversity of black shale types within the same framework. Previously, differences in the organic matter of different black shales have led to the supposition that there may have been many modes of formation of these deposits [Arthur et al., 1984]. However, we have seen that the thermohaline circulation, which governs the flux of marine organic matter to the sediment interface, is a relatively minor control on deep water oxygenation. Therefore, it would not be surprising that within the continuum of climatic change that resulted in anoxia, there should be occurrences in which upwelling rates were relatively large, as also pointed out by

Southam et al. [1982]. Similarly, it would not be surprising that there should be anoxia associated with low-productivity episodes such as those postulated by Bralower and Thierstein [1984], though our model shows, contrary to their model-based conclusions, that such episodes can occur in the presence of quite substantial deep water formation rates. Black shales of the Cenomanian-Turonian anoxic episode (for example, DSDP sites 105, 550B, Italian "Bonarelli horizon") which generally contain high concentrations of marine organic matter [Arthur et al., 1987] and high silica concentrations [Arthur and Premoli Silva, 1982], display 20-kyr and 100-kyr rhythms in redox state which are very similar to the Albian black shale cycles in the Italian site, which Pratt and King [1986] have determined to contain primarily terrestrial organic matter. In the former case, marine organic carbon flux overwhelmed deep water oxygen supply; in the latter, only relatively degradation-resistant organic matter was preserved under low-productivity conditions. Such variability records the partial decoupling of low-latitude marine productivity from controls on deep water oxygenation.

Of course, if the ratio of nutrient content to dissolved O_2 of the oceans were higher during the Cretaceous, the sensitivity to the upwelling overturning term (T) would be increased (Figure 5a). Perhaps the greater propensity toward anoxia in the Cretaceous is indicating that this ratio was indeed higher on the average. A proper examination of this issue requires that we develop a more quantitative understanding of what controls nutrient levels in the present ocean, a problem which still remains to be tackled.

A final comment concerns the implications of including a thermocline box or set of boxes in our model following the approach of Knox and McElroy [1984] and Boyle [1986]. The consequence of including a thermocline box is that it is possible to shift nutrients from thermocline depths into the deep ocean by increasing the fraction of organic material which is oxidized at depth and/or decreasing the exchange between the deep ocean and the rest of the ocean; or to shift nutrients from the deep ocean into the thermocline by the reverse of these processes. A shift of nutrients within the ocean will have a significant impact

on oxygen levels; the oxygen will be lower where the nutrients are higher and one might thus find that a portion of the water column could be driven to anoxia by concentrating nutrients there (which is what causes the present oxygen minimum), or that the locus of anoxia could shift quite dramatically in depth. The shifts required to cause extensive anoxia are extremely large. For example, if one takes an ocean 4 km deep with a mean oxygen level of 168 $\mu\text{mol/kg}$, which means that approximately 325-168 = 157 $\mu\text{mol/kg}$ of oxygen has been utilized in the remineralization of organic matter, one would require that 100% of the oxygen utilization occur in half the ocean (2 km) in order to drive that half anoxic. On the other hand, the shifts required to drive a narrower band to anoxia are proportionately smaller.

CONCLUSIONS

The major conclusion we draw in considering the global ocean is that episodes of anoxia may be only weakly associated with global surface productivity and/or the rate of upwelling/thermohaline overturning. We have shown that the deep ocean oxygen is controlled primarily by the magnitude of the direct exchange between the high-latitude surface regions and the deep ocean which feeds fresh oxygen into the abyss, relative to the export of organic matter by organisms in these areas, which creates an oxygen demand in the abyss.

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