

REDOX ZONATION IN THE PHANEROZOIC ANOXIC OCEAN

Part I.: Chemical Oceanographic Model

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ABSTRACT

Five principal redox zones in the open ocean: Oxic, Nitric, Sulfatic, Carbonic, and Nitronic are proposed based on the sequential thermodynamic availability of electron acceptors needed to oxidize marine planktonic organic matter. This is a chemical oceanographic refinement of the physical oceanographic model of redox conditions presented in Wilde [1987]. A sequence of such chemical zones may have been present in the ancient ocean when anoxic conditions were more common before the ventilation of the ocean with biogenically derived atmospheric oxygen and periodically since then, due to a combination of extended warm climatic intervals, poorer oceanic circulation and separation of basins from the global ocean. Maintenance of individual redox zones in the water column would occur in the pycnocline, where maximum stability and stratification are found. The redox boundaries in terms of equivalent oxygen for each zone is a function of the reservoir of available oxidant and amount of

reducing agent as planktonic organic matter and is calculated in terms of modern sea water chemistry. Generic formulae are given so that equivalent oxygen values can be calculated for varying oxidant reservoirs of the past. Equivalent oxygen values at the boundaries can be substituted into redox profiles with depth to obtain the thickness of each zone. The intersection of the various zones with the bottom would create different initial interstitial water chemistries for diagenetic water-sediment interactions, which may be discernible in the geologic record.

INTRODUCTION

Interest in anoxia in the water column has been generated through investigations of the origins of various "black" shales or sapropels in the general geologic record [Demaison and Moore, 1980] and particularly in the Paleozoic [Berry and Wilde, 1978] and in the Mesozoic [eg. Arthur and Schlanger, 1979; Arthur, Schlanger and Jenkyns, 1987; Brass et al., 1982; Hallan, 1981, 1986; Jenkyns, 1980; Ryan and Cita, 1977; Southam, Peterson, and Brass, 1982; Wilde and Berry, 1982]. Paleontologists and paleoecologists also have become interested in low oxygen to anoxic environments through reinterpretation of both ancient and modern biofacies [Rhoades and Morse, 1971; Byers, 1977; Thompson et al., 1985; Savrda and Bottjer, 1987; Berry, Wilde, and Quinby-Hunt, 1987]. Concurrently, chemical and biological oceanographers have sampled and analyzed modern low oxygen or true anoxic marine and estuarine conditions [eg. Anderson et al., 1982; Cline and Richards, 1972; DeVol, 1978; Fanning and Pilson, 1972; Hashimoto et al., 1983; Saino et al., 1983; Redfield, Ketchum, and Richards, 1963; Richards, 1965, Thomas, 1966; Weiss, 1970]. Physical oceanographers have investigated the conditions for the formation of the oxygen minimum [Riley, 1951; Wyrтки, 1961, 1962; Taft, 1963; Arons and Stommel, 1967; Wooster, 1967; Warren, 1981]. Unfortunately, because anoxic conditions in the modern well-ventilated ocean are limited areally, modern oceanographic interpretations only can be indicative with respect to the formation and maintenance of true oceanic anoxic

conditions in ancient oceans. Furthermore, there is no real "fossil" seawater as a check. Accordingly, the rock record must be interpreted through the screen of diagenesis and lithification and even metamorphism to assess the ambient conditions of sea water during deposition. However, modern oceanographic studies and the rock record in conjunction with accepted physical, chemical and biological principles can be used to provide working models of anoxic conditions of the past.

Wilde [1987] has described a physical oceanographic model for the ventilation of the open ocean as a result of the increase of atmospheric oxygen from non-existence to low levels in the Precambrian to its present concentration. Assuming that the exchange of oxygen between the atmosphere and the oceans is governed by Henry's Law, then the oceans potentially were anoxic below the surface wind-mixed layer, a function of the (a) atmospheric concentration of oxygen; (b) primary productivity in the surface waters; (c) temperature and oxygen content of the constituent water masses; and (d) stability and vertical advection both in the pycnocline and in the deep isothermal layer.

This is the first in a series of papers on potential paleo-oceanographic anoxic conditions, expanding on the discussion in Wilde [1987], with the goal of presenting the oceanographic, biologic and geologic conditions that produce anoxic waters, sediments and biofacies through time. This paper presents a thermodynamically-based chemical oceanographic model, which adds a chemical dimension to the physical oceanographic model of Wilde [1987]. Future papers will discuss the interaction of these models with the sea floor and marine sediments and resulting paleo-oceanographic significance.

OCEANOGRAPHIC EVIDENCE FOR ANOXIC ZONATION

The modern open ocean is well-ventilated with oxygen so that regions of true anoxic conditions long were thought to be limited to small areas of restricted circulation such as silled basins [Deuser, 1975, p.2] as the Black Sea, the Gotland Deep, and the Cariaco Trench as well as fjords such as "Lake" Nitinat [Richards, 1965; Fanning and Pilson, 1972; Grasshoff, 1975; Scranton et al., 1987]. Chiefly by analogy with the modern Black Sea and restricted basins, most earth scientists consider anoxic conditions to be synonymous with sulfidic or reduced sulfur waters [see Ryan and Cita, 1977]. Accordingly, usually only two types of water masses, oxic and anoxic; but four types of biofacies (1) aerobic [$>1 \text{ mL/L}$], (2) dysaerobic [0.2 to 1 mL/L]; (3) exaerobic [0.2 to 0.1 mL/L]; and (4) anaerobic [$< 0.1 \text{ mL/L}$] [Rhoades and Morse, 1971; Byers, 1977; Savrda and Bottjer, 1987] based on redox potential are considered in environmental interpretations. Even in sulfidic waters in modern restricted basins, the redox potential is not uniform. Based on the deviation of the sulfate/chlorinity ratio from that of the conservative open ocean and absolute concentration of sulfide, the Black Sea is more reducing than the Cariaco Trench [Deuser, 1975, p. 13-15; Kremling, 1974, p. 153]. The Black Sea is not a true open ocean analog as its density structure is determined by salinity rather than temperature variations so that the pycnocline, in the Black Sea, is similar to the halo-cline. However, the Black Sea has a transition layer (redoxocline) embedded in the halocline, between surface oxic conditions and deep reducing conditions which varies seasonally and geographically between 120 and 300 meters [Stoyanov, 1986]. Increasing field evidence from the modern ocean also suggest that such a two-fold oxic-anoxic zonation is too simple and that the transition layer between oxic and sulfide rich waters is relatively thick in vast areas. In fact, the volume of "zero" oxygen water at the oxygen minimum is more extensive than previously thought due to errors in Winkler determinations at low oxygen concentrations [Broenkow and Cline, 1969; Cline and Richards, 1972]. Thus, extensive anoxic and low oxygen portions of the modern open ocean have redox zones not governed by reduced sulfur species.

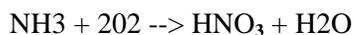
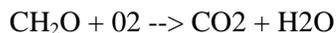
Such non-oxic but also non-sulfidic waters as found in the 100 m thick "oxygen minimum zones" extending hundreds of kilometers offshore in the

Eastern Tropical Pacific [Brandhorst, 1959; Anderson et al., 1982]. Here in the pycnocline, denitrification and nitrogen reduction, not oxygen reduction are the major processes consuming organic matter below the oxic zone [Broecker and Peng, 1982, p. 141]. In the Arabian Sea, extensive areas, up to about 800 m thick, with no oxygen and exceptionally high nitrite occur at intermediate depths and even extending to the bottom in northern regions [Deuser, 1975, p. 10; Qasim, 1982]. Hydrogen sulfide also was reported by Ivanenkov and Rozanov [1961]. In the modern Eastern Tropical Pacific ocean due to ventilation of deep water as a result of the present cold climate, the nitrate reduction zone is underlain by a nitrification zone produced by oxygen advecting from below with no substantiated sulfate reduction zone [Anderson et al., 1982]. Apparently, there is sufficient organic productivity in excess of ventilation in the Indian Ocean for the core of Arabian Sea to support sulfate reduction; although subsequent expeditions could not find sulfide [Qasim, 1982, p. 1049]. Geologically such conditions could obtain during warmer climates and prior to the complete ventilation of the ocean when deep waters were not reoxygenated to the extent they are during present cooler glacial climates.

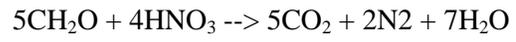
CHEMISTRY OF ANOXIA

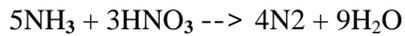
Redfield, Ketcham, and Richards [1963, p 42-43] noted that with the depletion of oxygen due to consumption by organic matter, other constituents in sea water replace oxygen as the electron acceptors. They suggested the principal redox reactions in modern sea water were:

Oxidation by oxygen

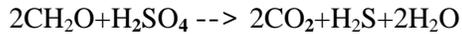


nitrification



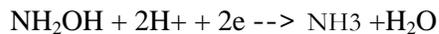
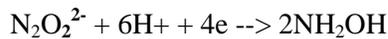
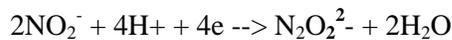
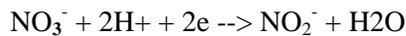


Sulfate Reduction



No oxidation of NH_3

For the nitrogen system, Vaccaro [1965, p. 175] designated the steps in the assimilation of nit-rate by algae as:



The sequence of oxidizing agents at increasingly lower pe (Table 1 and Appendix A) is observed in digester reactions in municipal waste treatment plants [Stumm and Morgan, 1970, p. 336-337]; chemotrophic bacteria [Fenchal and Blackburn, 1979, p. 79; Blackburn, 1983]; and the diagenesis of anoxic sediments [Berner, 1981, Froelich et al., 1979]. These situations are analogs of conditions in an ocean without deep-ventilation or in which there always is excess organic matter. The analogs are fundamentally sediment-bacteria reactions [Krumbein and Swart, 1983] with boundaries determined by Fickian diffusion [Berner, 1980]. That redox sequence applies to the more fluid open ocean case if the vertical transfer approaches the values of Fickian diffusion as observed for the oxic/anoxic transition in Lake Nitinat [Broenkow, 1969]. In other words, the redox sequence applies if vertical mixing is small and vertical advection is on the order of molecular diffusion. This would occur at strongly density-stratified boundaries. In the present ocean such strong stratification is seen at the boundaries of the main oceanic pycnocline or compressed in local situations such as the Black Sea or fjords like Lake Nitinat.

CHOICE OF SIGNIFICANT ELECTRON ACCEPTORS IN SEA WATER

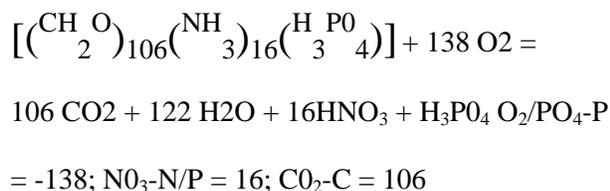
The three principal redox zones of Redfield, Ketchum, and Richards [1963, p. 43] for the modern ocean have been extended to ancient oceans. The five major zones are identified by the principal oxidant: (1) OXIC zone-dissolved oxygen gas; (2) NITRIC zone-nitrate; (3) SULFATE zone-sulfate; (4) CARBOXYLIC zone-carbon dioxide; and (5) NITRONIC-dissolved nitrogen gas. Appendix A gives a detailed description of these zones. Theoretically any electron donor would react in its proper thermodynamic sequence if present in sea water. The major dissolved species because solid particles or minerals would have a relatively rapid transit time through the water column [Stumm, and Bruland, 1979; Honjo, 1982]. Thus, the influence of mineral composition in redox reactions predominates in bottom sediments. Therefore, the major redox zones in the water column are not necessarily the same as described in sediments. During the last 20 years, such as Fe and Mn in common marine minerals are reduced by reactions with organic matter [Froelich et al., 1979; Krumboltz, 1982]. The free energies for reduction of manganese minerals (-3090 to -2920 kJ/ mole glucose) would place these reactions in less reducing conditions than sea water; and for iron minerals (-1410 to -1330 kJ/ mole glucose) in the more reducing part of the Nitric zone just above the Oxic zone. The dissolved content of these metals in sea water: $Fe_{\text{mean}} = 0.0007$ pmoles/kg; $Mn_{\text{mean}} = 0.0002$ pmoles/kg [Quinby-Hunt, 1982]. Thus, they would have much direct influence on the redox state of sea water other than as indicators.

DEFINITION OF ANOXIC ZONES

Zonation of the anoxic values is in sequence of decreasing pE (Appendix A) emphasizing electron-acceptor systems. The zonation is presumably similar to those since the Late Precambrian and Lower Paleozoic. For this discussion, modern concentrations are used (Table 2) considering that the atmospheric concentration of oxygen had reached its current level of approximately 21% by the beginning of the Phanerozoic [Cloud, 1976; Budyko, Ronov, and Yanshin, 1987] do not change as there is free oxygen in the atmosphere. Nitrogen compounds, NO_3^- and NO_2^- , are derived from oxidation of ammonia. The available ammonia in the photic zone is taken up by phytoplankton [Eppley, Rogers, and McCarthy, 1969]. At present, the nitrate and nitrite produced by nitrifying bacteria is converted to N_2 [Stumm and Morgan, 1970, p. 336, eq. B] during denitrification. Thus, they accumulate in sea water except from the oxidation of plankton at the lower pE levels found with increasing depth.

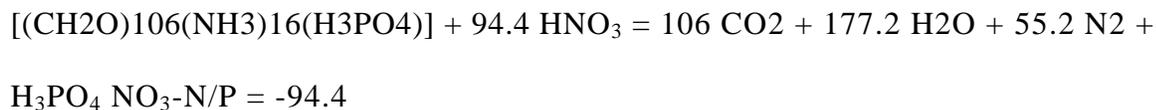
For comparison with the oxidizing power of oxygen, other non-oxygen oxidants can be assigned negative oxygen values. [1963] describe an "oxygen equivalent" based on the stoichiometry of [P] or [H₃PO₄] in plankton with respect to various oxidants [446-447]. In essence, the amount of H₃PO₄ released by oxidation of plankton by oxidants other than oxygen is equated to the amount of H₃PO₄ generated the same amount of H₃PO₄. The stoichiometry for the model in order of increasing anoxicity, using plankton as the

OXIC CONDITIONS

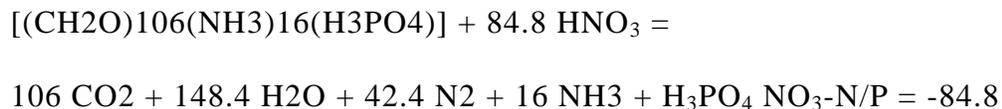


ANOXIC CONDITIONS

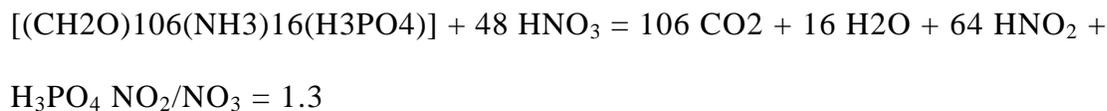
1 a. Denitrification via Nitrate



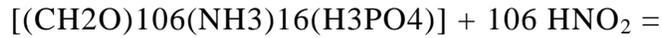
1b. Denitrification via Nitrate



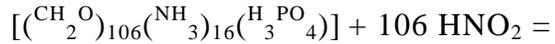
2. Nitrite Formation



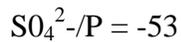
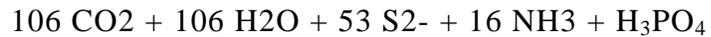
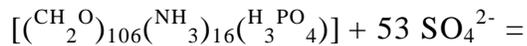
2a. Denitrification via Nitrite



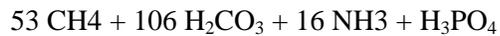
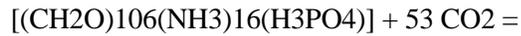
2b. Nitrite Reduction



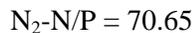
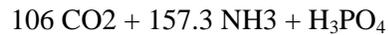
SULFATE REDUCTION



METHANE FERMENTATION



NITROGEN FIXATION



Accordingly,

[Oxidant as O_2 equivalent] $-138[H_3PO_4]$ generated [Wilde, 1987, P. 447];

for each step in the redox pathway. The sum of each step $E[H_2PO_4]$ will give "negative" oxygen concentration, which can be related to more familiar oxygen with depth profiles. Table 2 gives the lower boundaries of the redox zones in terms of oxygen equivalents. Potential oxidants with low concentrations in the present ocean such as Fe, Mn etc. are ignored (Table 1).

The approach used differs from that of Sillen [1961], Garrels and Perry [1974], and Krump and Garrels [1986] in that only the oceans and the atmosphere are considered and not the global equilibrium interactions among the atmosphere, hydrosphere, and lithosphere. That is, here the ocean is titrated with organic matter, as plankton, not with the reactive crust or minerals in sediments. Obviously, large deviations in the past from present oceanic concentrations, for example in the S, N, or Fe systems [Broda, 1975; Holland, 84; Holser, 1984] would change the predicted oxygen equivalents at the zonal boundaries and thus the depth/thickness of the zones. However, if such concentrations are "known" or can be derived from a model, they can be substituted for the modern concentrations.

Table 2 demonstrates the variability possible in the boundary between the Nitric and the Sulfatic zones or the thickness of the Nitric zone. This variability has evolutionary consequences due to the toxicity of sulfide from the Sulfatic zone to megafauna. A relatively thick Nitric zone would act as a barrier to toxic upwelling into the surface mixed layer, especially if the Nitric zone extends beyond or near the edge of the continental shelf. The situation could be further complicated by the addition of biologically monitored pathways involving N_2O_2 etc. as mentioned above [See Vaccaro, 1965]. Such a complication seems premature for a paleo-oceanographic model, which must include simplifying assumptions to permit comparisons with the imperfect geologic record. The difference of about -0.8 mL/L between the major pathways (Table 2) may seem small, but it is equivalent to about 15% of modern surface concentrations.

Consumption of the reservoir of sulfate as an oxidant present in the modern ocean would require enormous amounts of reducing agents as organic matter. Thus development of a Carbonic zone and a

Nitronic zone would be unlikely in the fluid open ocean in the Phanerozoic once the ocean had been ventilated in the Post-Devonian [Berry and Wilde, 1978]. Such reduced zones, however, might exist (I) as residuals prior to and during the ventilation of the atmosphere and ocean or (II) if there has been a vast reduction in the amount of dissolved sulfate in the oceans, for example due to evaporation and precipitation or extensively recycling through the ridge-rise systems [Bischoff, 1980; Rosenbauer and Bischoff, 1984; Seyfried and Janecky, 1985].

CHEMICAL CHARACTERISTICS OF MAJOR ZONES

The redox relationships within each zone bounded by pE or equivalent oxygen values determine the dissolved species availability. The type and availability of chemical species then govern both the equilibrium mineralogic and biologic reactions permitted which has both geologic and evolutionary implications.

The chemical characteristics of the Oxic zone are well documented with dissolved oxygen as the principal oxidant down to concentrations of about 9 $\mu\text{moles/kg O}_2$ (0.2 mL/L) [DeVol, 1978]. Reduced nitrogen compounds, such as ammonia would be oxidized to nitrate and dissolved metals such as iron and manganese would be respectively as Fe^{3+} and Mn^{4+} . As the oxygen concentration approach the lower limit, nitrate would approach maximum concentration.

With the cession of the oxygen oxidant system, nitrate becomes the most abundant oxidant typifying the Nitric zone. As shown above, there are various pathways available for the oxidation of planktonic matter in the Nitric Zone. In mildly anoxic conditions seen occasionally in the modern open ocean, presumably with dissolved but unoxidizing oxygen available, denitrification occurs depleting the nitrate and generating N_2 . Here, dissolved Mn is reduced so that manganese oxides are no longer stable. However, iron is still as Fe^{3+} . Ammonia from plankton also would be oxidized during denitrification. At lower pE , any remaining nitrate would be reduced to nitrite. This nitrate initially would be used in further denitrification. At slightly lower

pE , ammonia would begin to increase in the water column not only by reduction of nitrate but by release from decaying plankton. In this stage, therefore, oxidized nitrogen compounds are consumed (Appendix A). Trace amounts of dissolved U, dissolved organic carbon (DOC) and Fe would be the next available oxidants. However, their concentrations are so low, it is unlikely they could maintain a distinct zonation and would act as indicators with ferrous rather than ferric iron being stable. Ammonia would continue to increase through the decay of plankton adding to the alkaline buffer of sea water.

The Sulfatic zone, due to the large reservoir of sulfate, would be a major anoxic zone. With decreasing pE , more reduced sulfur species would be produced as planktonic matter is oxidized. The relative concentration of reduced-sulfur species such as sulfite, thiosulfate, elemental sulfur to sulfide present in proportion to the declining concentration of sulfate, as a function of p_c , is complicated by microbial mediation [Krumbein and Swart, 1983]. Such biological influence would be important at stratified boundaries, such as the base of the mixed layer-top of the main pycnocline, where microbes could concentrate on relatively buoyant large organic particles. At the appropriate concentration of sulfide, both iron and manganese and other sulfides would precipitate depleting the water column of these metals. As the concentration of metals is low compared to the amount of sulfide generated, precipitation of sulfides and depletion of metals would occur near the Nitric-Sulfatic boundary at relatively high p_c . Also, ideally large amounts of carbon dioxide (Table 2) are generated by oxidation of planktonic organic matter by sulfate. It is unlikely such concentration of dissolved CO_2 can be maintained without outgassing to the atmosphere particularly during non-glacial climates when the mean oceanic temperature was warmer. At a minimum, the Sulfatic zone would be saturated with CO_2 . Ammonia would continue to be released through the oxidation of plankton. The presence of ammonia might buffer the pH countering the acidity of the reduced sulfur species and $[CO_2]$. This adds to the complexity of the pH-alkalinity question for ancient oceans, which is beyond the scope of this discussion

After consumption of dissolved sulfate, dissolved carbon dioxide would be the next oxidant signifying the Carbonic zone. This zone is characterized by generation of methane and the continued addition of ammonia.

The depletion of CO₂ with the presence of ammonia would reverse the tendency for lower pH developed in the Sulfatic zone.

The last potential abundant oxidant is dissolved N₂, which at very low pc, would be reduced to ammonia in the Nitronic zone. In microbial buffered systems, nitrogen fixing is common and thus could occur at highly stratified boundaries but most likely at the water-sediment interface.

MAINTENANCE OF DISCRETE ZONES

In the pycnocline, mixing between anoxic zones would be governed by the stability of the water column. Wilde and Berry [1984, p. 146-148] discussed the stability in terms of static stability: E [Sverdrup, 1915]; buoyancy frequency: N [Gill, 1982, p. 51-52]; and the Richardson number: Ri [Munk, 1966, p. 710] for three climates [Wilde and Berry, 1982] {see Table 3}. Brass, Southam, and Peterson [1982] used a buoyancy flux, (the mass flux times the negative of the square of the buoyancy frequency) to model "ventilation" which is a function of the mass flux or the rate of water mass formation. Vertical advection in the modern (glacial) ocean is about 1 to 3 X10⁻⁷ meters/second [Warren, 1981, p. 785] or about 3 meters/year, which is slow enough to permit organic matter to rain down from the photic zone into the pycnocline where it is oxidized. Vertical advection in warmer climates should be lower with less of a density contrast in thermally formed water masses as thus slower rates of global overturn.

In the ancient ocean, the density profile in the main pycnocline may have been more complex. Particularly during milder climates [Wilde and Berry, 1984, Brass, Southam, and Peterson, 1982], there may have been multiple pycnoclines with additional strongly stratified boundaries reflective of multiple sources of water masses. Under such conditions, each zone would have a thickness related to the volume and stability of the water mass with respect to that of overlying and underlying water masses in the main pycnocline. The type of zone (the oxidant in thermodynamic sequence which is the electron acceptor) at any given depth would be a function of the amount of organic material remaining and the amount of electron

acceptors. In any case, stability restricted vertical advection associated with density stratification is required to permit formation of discrete anoxic zones. Otherwise, the water would be homogenized with relatively uniform properties as seen in the modern surface mixed layer and deep ocean water masses. Accordingly, for the chemical model discussed here, the various anoxic layers are considered embedded in the main pycnocline which has significant vertical extent. Within each zone, the concentration of the principal oxidant would decline as a function of the consumption of organic matter in a manner similar to that observed in modern oxygen profiles in the pycnocline.

As shown in Table 3, the highest stability (E) would be during glacial times; although the thickness of the pycnocline would be the least. The greatest potential for development of discrete zones would be during non-glacial times with the thickest pycnocline and lowest vertical advection from deep water as a result of slower deep circulation. However, the stability would be the lowest and internal circulation within the pycnocline could homogenize some of the smaller oxidant reservoirs within the major zones. Wilde [1987], using Wyrтки's [1961, 1962] vertical ventilation models modified for anoxic conditions, showed that anoxia is not necessarily vertically symmetric within the pycnocline and varies with both the overlying productivity and relative redox state between the upper mixed layer and the deep water. Due to the large reservoir of sulfate in seawater, it is unlikely that increased productivity in the *open* ocean could produce any zone more anoxic than the Sulfatic with any appreciable oxygen in the atmosphere and vertical advection of oxidants from ventilated deep waters, as the maximum anoxicity at 1% PAL is only -12 mL/L O₂ [Wilde, 1987, p. 450]. However, such a situation is a dynamic one for an interconnected world ocean with longitudinal temperature differences generating inter-tonguing water masses of varying densities.

Given various paleogeographic reconstructions with opening and closing oceans such as proposed for the Cretaceous Proto-Atlantic or the Paleozoic Iapetus, interconnections of geologically large basins with the global ocean could be limited to non-existent. For a closing ocean with initial normal oceanic salinity and chemistry, the effect could be increasing stagnation and diminishing deep circulation. This would permit an increase in the maximum value of the anoxicity given excess organic matter. Due to shoaling, and

the increased surface area to volume connection with the atmosphere, it is unlikely that Carbonic or Nitronic zones could develop. However, if the sulfate content was reduced by precipitation of evaporitic sulfates, more anoxic conditions are possible. For an opening proto-ocean, the initial "sea water" chemistry could be vastly different from that of the global ocean. Particularly if the sulfate content was low and productivity high, the Carbonic or even the Nitronic zones could develop. Accordingly, for ancient marine basins with limited or no interconnection to the global ocean, the values in Table 2 could be lower and numerous anoxic zones may exist.

As noted above, in the modern ocean a vertical gradient of redox zones beyond three is seldom observed and, where found, such zones are embedded in the pycnocline. In the presence of excess organic matter, anoxicity usually results in the generation of sulfide due to the large reservoir of sulfate with respect to the small amount of nitrate and nitrite. However, if the organic matter is oxidized prior to attaining the p_e of sulfate reduction, the level of anoxicity (p_e) could be maintained at the level at which the organic matter was consumed. In this situation with no effective ventilation from below, the minimum p_e at a given depth would be controlled by amount of reducing agent at that depth rather than the concentration in sea water of the oxidant. Under regions of low productivity, waters less anoxic than the Sulfatic zone could develop in the region of minimum vertical advection in the main pycnocline. The thickness of these zones probably would vary latitudinally as does the modern pycnocline. The present oxygen minimum "denitrification" zone off Peru is about 100 m thick [Anderson et al., 1982] and is located in the most stable portion of the pycnocline at the base of the surface mixed layer. Based on the present "oxidant" budget in the modern ocean, there is about 1000 times as much sulfur and carbon available as there is oxidized nitrogen (Table 2). This may explain the thin nitrate reduction zone in the modern ocean. In the Black Sea, chemosynthesizers consume nitrate and nitrite so that sulfate reduction can begin just below the oxic/anoxic boundary where the pycnocline is compressed vertically as a fresher water-sea water interface [Grasshoff, 1975]. Thus the chemical situations examined here, place the maximum gradient of anoxicity in the most stable part of the

water column in the pycnocline.

INTERACTION OF REDOX ZONES WITH BOTTOM SEDIMENTS

Froelich et al. [1979] have developed a technique to examine diagenetic reactions in the modern ocean starting with concentrations in the overlying water. Their methods can be used in conjunction with the redox zones proposed here, by changing the concentrations in the overlying water to match that in the appropriate redox zone. Frakes and Bolton [1984] suggested such a procedure to explain the transfer of manganese between oxic and anoxic waters related to changes in sea level. Thus the proposed redox zonation of ocean might be used as initial bottom water chemistries in conjunction with marine rocks to quantify paleo-oceanographic conditions using the various chemofacies models of Borchert [1965]; Froelich et al. [1979]; and Berner [1980]. A detailed discussion of this marine geochemical approach will be presented in a subsequent paper in this series.

LIMITATION OF THE MODEL

The chemical model is used to relate such profiles to an oxidation-reduction hierarchy used to specify significant redox zones. Any interpretations based on their use should consider the following limitations and assumptions.

a. The model is based on a thermodynamic sequence without consideration of kinetics. The sequence used, however, is followed by bacteria for conditions of excess organic matter, which indicates feasibility.

b. The sequence assumes oxidation of excess organic matter, generated in the photic zone, which sinks vertically through the surface mixed layer into the pycnocline. Accordingly, horizontal advection of organic matter is ignored so the model is two dimensional. Whether this sequence is followed in reverse by

ventilation from deep waters below the pycnocline is not considered [see Stumm and Morgan, 1970, p. 337]. However, the model should be valid for most situations in the geologic record, where shelf seas and upper continental margin conditions obtain.

c. In the photic zone, the oxygen concentration is fixed at Henry's Law value of saturation. That is, consumption of oxygen by organic matter is ignored in the upper 50 m and reduction begins only below the photic zone. This condition is to satisfy the conditions of the physical oceanographic model [Wilde, 1987].

d. Modern concentrations are assumed for major oxidants such as nitrate, and sulfate. Alternate pathways could be chosen particularly with respect to the nitrogen system. In the model, oxidized nitrogen compounds were derived initially from plankton (oxidation of ammonia by oxygen). This assumes no oxidized nitrogen at the surface. Subsequent oxidation of plankton by nitrate could yield nitrogen gas, as in conventional denitrification, but also nitrite or N_2O_2 . Conversion to nitrogen gas may occur in the photic zone at high pc. Due to uptake of nitrogen compounds by phytoplankton, nitrate and nitrite concentrations are near zero near the surface. Accordingly, some oxygen may be consumed that does not contribute to the production of nitrate. However classic denitrification does not occur with depth in some areas in the modern ocean (Peru, Eastern Tropical North Pacific, Arabian Sea) where nitrite accumulates at lower pc. Allowance for denitrification would reduce the amount of nitrite generated in a secondary pathway. Accordingly, zonation using oxidized nitrogen compounds such as nitrate and nitrite may not be valid for either (1) an early low oxygen atmosphere where was insufficient oxygen to oxidize ammonia to nitrite or nitrate or (2) for the contemporary well-ventilated ocean due to denitrification to unreactive nitrogen gas. The result would be to shrink a combined Nitrous and Nitric zone and shift the boundary of the Sulfatic zone to a more positive oxygen equivalent value.

e. Ammonia is only oxidized by oxygen or nitrate during denitrification. In the absence of oxygen, ammonia from decomposition of plankton remains as ammonia. Any ammonia forming in the photic zone would be recycled back into phytoplankton. However, any ammonia forming below the photic zone could

concentrate in sea water below the appropriate pE.

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APPENDIX A

Chemical Zones in Sea Water

A model of redox zones in the open Ocean is proposed based on the oxidation of excess plank-*tonic* organic matter stoichiometrically in the ratio of C:N:P = 106:16:1 or $\text{CH}_2\text{O}_{106}(\text{NH}_3)_{16}(\text{H}_3\text{PO}_4)$ [Richards, 1959,1965]. The principal reducing reactions, considered on the basis of the transfer of one electron are:



$$pE^\circ(\text{W}) = -8.2$$



$$pE^\circ(\text{W}) = +6.2$$

The successive redox zones, described below, from oxic through increasing stages of anoxicity are defined by characteristic electron acceptors (oxidants) in thermodynamic order or decreasing pE [Stumm and Morgan, 1970, p. 318, 1985] at $\text{pH} = 7$ and within the stability field of water. Free energies are calculated in the manner of Froelich et al. [1979]. Oceanic concentrations used are from Quinby-Hunt and Turekian [1983]. To impart the maximum information in describing the major zones, a nomenclature is proposed giving the oxidant, as an adjective, and the reactant and reduced product as nouns. Indicator reactions within the major zones are designated by the element

involved.

1. *OXIC: oxygen-*

Saturation with air down to about 10 $\mu\text{mole/L O}_2$ [Devol, 1978], this is the present open ocean case with oxygen as the oxidant. Governing reaction:



$pE^\circ(\text{W})$ Oxidant (Eq. 4) = 13.75

$pE^\circ(\text{W})$ Reaction (Eq. 1 & A) = 21.95

Free energy of reaction = -3006 KJ (-718 KCal)/mole glucose.

Mean Oceanic Abundance: $\text{O}_2 = 150 \mu\text{mole/Kg}$ Mean Surface Abundance: = 205 $\mu\text{mole/Kg}$

2. *NITRIC: nitrate-nitrite/nitrogen/ammonia*

Some non-reactive oxygen (less than 10 $\mu\text{mole/L}$) may be present in the higher pE end of the zone as seen in the present "oxygen minimum zone" seen off Peru, Costa Rica, and in the northern Indian Ocean. The zone effectively begins with the decline in nitrate concentration and the appearance of the significant nitrite. As discussed in Stumm and Morgan [1970, p. 330-332], simple correlation of the thermodynamics of the nitrogen system with the observed concentration in modern natural aqueous environments is not justified. Nitrogen gas is not converted to nitrate in the well oxygenated surface waters and at lower pE denitrification apparently proceeds indirectly by initial reduction of nitrate to nitrite then reaction of nitrite with ammonia to produce nitrogen gas. Thus in the photic zone, if ammonia is consumed by organisms, denitrification may be suppressed. In this model, following Stumm and Morgan [1970, p. 331, Fig. 7-9b] the dominant nitrogen species shift with declining pE . This assumes

that the p_c drops fast enough that denitrification does not substantially deplete nitrite. Thus the governing reaction is (2b); although the other nitrogen reactions are given in their proper order:

2a. *Denitrification* (reduction of oxidized nitrogen compounds)

The high p_e of this reaction and the gap in p_c between step 2a and step 2b suggest denitrification might be included in the Oxic zone. If so an alternative first anoxic step would be manganese reduction (pyrolusite) with a $pE^\circ(W)$ of 16.35 (see step 2c below). Denitrification is included here in the Nitric zone as nitrate is the oxidant.



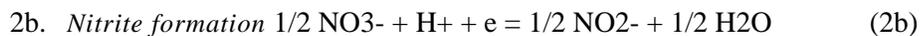
$$pE^\circ(W) \text{ Oxidant (Eq. 5a)} = 12.65 \qquad pE^\circ(W) \text{ Reaction (Eq. 2a1 \& A)} = 20.85$$

Free energy of reaction = -2855 KJ (- 682 KCal)/mole glucose



$$pE^\circ(W) \text{ Oxidant (Eq. 5a}^+) = 12.33 \qquad pE^\circ(W) \text{ Reaction (Eq. 2a2 \& A)} = 20.53$$

Free energy of reaction = -2811 KJ (- 671 KCal)/mole glucose



$$pE^\circ(W) \text{ Oxidant (Eq. 5b)} = 7.15 \qquad pE^\circ(W) \text{ Reaction (Eq. 2b + A)} = 15.35$$

Free energy of reaction = -2101 KJ (-502 KCal)/mole glucose.

Mean oceanic abundance: $\text{NO}_3^- = 30 \mu\text{moles/Kg}$ Mean

Surface Abundance: $= \text{NA? } \mu\text{mole/Kg}$

2c. *Manganese Reduction*

Using solid phase birnessite as indicative of dissolved species with lowest pe. If values for pyrolusite used in computation, then this zone would be included between 2a and 2b.



$\text{pe}^\circ(\text{W})$ Oxidant (Eq. 2c) = 8.15: pyrolusite to 6.7: birnessite

$\text{pe}^\circ(\text{W})$ Reaction (Eq. 2c & A) = 16.35: pyrolusite to 14.9: birnessite

Free Energy of reaction = -2040 KJ (-487 KCal)/mole glucose: birnessite. Mean

oceanic abundance: $\text{Mn} = .0002 \mu\text{moles/Kg}$

Mean Surface Abundance: $= .0006 \mu\text{moles/Kg}$



$\text{pe}^\circ(\text{W})$ Oxidant (Eq. 2d) = 6.15

$\text{pe}^\circ(\text{W})$ Reaction (Eq. 2d & A) = 14.35

Free energy of reaction = -1965 KJ (-470 KCal)/mole glucose

2e. *Nitrite reduction: nitrite-ammonia*

Reduction of nitrite to ammonia with release of ammonium/ammonia from organic matter. Such a step is not seen in the modern open ocean due to advection of oxygen from deep water

(nitrification). Concentration of ammonia could occur in this zone and the preceding zone 2d, if below the photic zone. Governing reaction:



pE°(W) Oxidant (Eq. 2e) = 5.82

pe°(W) Reaction (Eq. 2e & A) = 14.02

Free energy of reaction = -1920 KJ (-459 KCal)/mole glucose.

Maximum oceanic abundance: NO₂⁻ = 10 pmoles/Kg

N₂ = 590 pmoles/Kg

NO₃⁻ = 30 pmoles/Kg



pE°(W) Oxidant (Eq. 2f) = 0.88

pe°(W) Reaction (Eq. 2f & A) = 9.08

Free Energy of reaction = -1243 KJ (-297 KCal)/mole glucose

Mean oceanic abundance: .013 μmoles/Kg

2g. *DOC as CH₂O-methane*

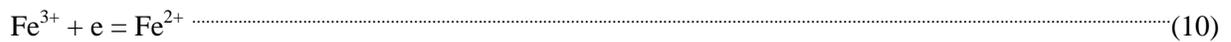
Auto-oxidation of dissolved organic matter (DOC) from organic productivity of plankton CH₂O to methane.



Free Energy of reaction = -1114 KJ (-266 KCal)/moles glucose Mean

oceanic abundance: DOC = 25 pmoles/Kg [Williams, 1975]

2h. Iron Reduction



$pE^\circ(W)$ Oxidant (Eq. 2h) = -1.67

$pE^\circ(W)$ Reaction (Eq. 2h0 & A) = 6.53

Free Energy of reaction = -894 KJ (-214 KCal)/mole glucose

Mean oceanic abundance: Fe = .0007 pmoles/Kg

Mean Surface Abundance: .00014 pmoles/Kg

3. SULFATIC: sulfate-sulfide

a. Sulfate reduction by bacteria yielding reduced sulfur species. Source of the sulfate is from sea water.

Governing reaction:



$pE^\circ(W)$ Oxidant (Eq. 3) = -3.75

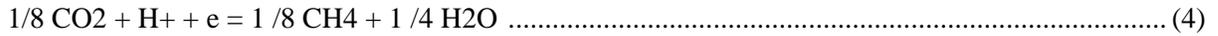
$pE^\circ(W)$ Reactant (Eq. 3 & A) = 4.45

Free energy of reaction = -380 KJ (-91 KCal)/mole glucose.

Mean Oceanic Abundance: SO_4^{2-} = 28,250 pmoles/Kg

4. *CARBONIC: carbon dioxide-methane*

a. Dissolved carbon dioxide from the dissolved carbonate system is reduced to methane producing a second zone of methane concentration. Additional CO₂ developed by the oxidation of plankton is used to oxidize additional organic matter. Unlikely to develop in the Proterozoic and later oceans due to the presence of oxygen in the atmosphere and the large abundance of dissolved sulfur species. Governing reaction:



pE°(W) Oxidant (Eq. 4) = -4.11

pE°(W) Reaction (Eq. 4 & A) = 4.07

Free energy of reaction = -557 KJ (-133 KCal)/mole glucose.

Mean Oceanic Abundance: CO₂ = 2200 μmoles/Kg.

5. *NITRONIC: nitrogen-ammonia*

Dissolved Nitrogen gas is reduced to ammonia. This is accomplished by nitrogen-fixing bacteria, such as *Amminobacter*, in present sea water. The occurrence of this process in thermodynamic sequence is unlikely in any post Archean ocean due to the abundance of sulfur and carbon compounds higher in the hierarchy.



pE°(W) Oxidant (Eq. 5) = -4.68

pE°(W) Reaction (Eq. 5 & A) = 3.52

Free Energy of reaction = -482 KJ (-115 KCal)/mole glucose

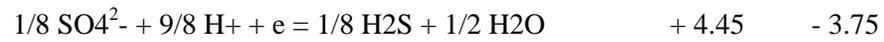
Mean Oceanic Abundance: N₂ = 600 pmoles/Kg.

TABLE 1

**SEQUENCE OF CHARACTERISTIC OXIDANT REACTIONS IN
SEA WATER BY ZONE**

	REACTION	$pe^\circ = \log K \quad pe^\circ (W)$	
I.	-OXIC-		
	$1/2 O_2(g) + H^+(W) + e = 1/2 H_2O$	+20.75	+13.75
II. a.	-NITRIC-		
	$1/2 NO_3^- + H^+ + e = 1/2 NO_2^- + 1/2 H_2O$	+15.35	+ 7.15
	* $1 / 2 MnO_2 + 2 H^+ + e = 1 / 2 Mn^{2+} + H_2O$	+14.9	+ 6.7
II. b.	-Nitrous-		
	$1 / 6 NO_2^- + 4/3 H^+ + e = 1 / 6 NH_4^+ + 1/3 H_2O$	+14.02	+ 5.82
	* $U^{6+} + e = U^{5+}$	+ 9.08	+ 0.88
H. c.	-Carboxylic-		
	$1 / 4 CH_2O + H^+ + e = 1 / 4 CH_4 + 1 / 4 H_2O$	+ 8.14	- 0.06
	* $Fe^{3+} + e = Fe^{2+}$	+ 6.53	- 1.67

III. **-SULFATIC-**



IV. **-CARBONIC-**



V. **-NITRONIC-**



Reactions modified from Stumm and Morgan [1970, p. 318]

See Appendix A

* Indicator reactions presumably not critical in sea water due to low concentrations of oxidant, but important in pore water reactions of marine sediments [See Froelich et al., 1979]

TABLE 2

LOWER BOUNDARIES OF REDOX ZONES
AS A FUNCTION OF OXYGEN EQUIVALENTS

ZONE	OXYGEN EQUIVALENT μ MOLES/kg	mL/L	EmL/L
OXIC			0.2
NITRIC ¹			
	Denitrification of nitrate pathway		
	138[HNO ₃]/84.8	-44	-0.96
			-0.96
	or		
	138[HNO ₃]/94.4	-39	-0.86
			-0.86
	Denitrification of nitrite pathway ²		
	138[HNO ₃]/48	-77	-1.69
			-1.69
	138[HNO ₂]/ 106	-46	- 1.00
			-2.69
	Nitrite reduction pathway ²		
138[HNO ₃]/48		-77	- 1.69
			-1.69

	$138[\text{HNO}_2]/106$	-46	-1.00	-2.69
SULFATIC ³	$138[\text{SO}_4]/53$	-73,530	-1606	-1607
CARBONIC ⁴	$138[\text{CO}_2]/53$	-5,310	-115	-1722
NITRONIC	$138[\text{N}_2]/70.65$	-12	-0.25	-1722

1. This assumes all nitrate is derived from oxidation of ammonia in plankton, with sufficient plankton available to consume the Henry's Law saturation value of oxygen or $[\text{HNO}_3] = 16[\text{O}_2]/138$. Thus for 230 pmoles/kg O_2 {approximate modern tropical concentration}, $[\text{HNO}_3]$ generated in the Oxidic zone = 27 pmoles/kg .

2. As the formation of $[\text{HNO}_2]$ from $[\text{HNO}_3]$ involves oxidation of additional $[\text{NH}_3]$, the $[\text{HNO}_2]$ generated is $1.3[\text{HNO}_3]$.

3. Modern oceanic $[\text{SO}_4] = 28,240$ pmoles/kg.

4. The modern concentration of 2039 pmoles/kg $[\text{CO}_2]$ ideally would be increased by oxidation of plankton by nitrate oxidation and particularly by sulfate reduction to 58,797 pmoles/kg. It is unlikely this amount of CO_2 would stay in solution [Harvey, 1957; Broecker and Peng, 1982], but would be outgassed into the atmosphere creating a new and higher saturation value. So the modern

value is used here.

TABLE 3

STABILITY CONDITIONS IN THE MAIN PYCNOCLINE

[after Wilde and Berry, 1982, 1984]

For a_z = vertical acceleration; g = acceleration due to gravity; z = vertical length; ρ = density, $S =$

CLIMATE:	Non-Glacial	Pre- or PostGlacial	Glacial
PYCNOCLINE			
THICKNESS:	2900 m	1400 m	900 m
<hr/>			
$10^8 E$ (meters ⁻¹)	43	84	523
$10^4 N/2\pi$ (Hertz)	3	4.5	11
$2\pi/N \times 60$ (minutes)	51	37	15
$10^4 \mu$ (seconds ⁻¹)	6	9	21

Static Stability: $E = -\frac{\alpha_z}{g} [\delta z] = \frac{1}{\rho} \frac{d\rho}{dz}$; For $E < 40 \times 10^{-8}$ $E = \frac{\alpha\rho}{\alpha S} \frac{dS}{dz} + \frac{\alpha\rho}{\alpha t} \left[\frac{dt}{dz} - \frac{d\theta}{dz} \right]$

Buoyancy Frequency: $N = \sqrt{gE}$

Richardson Number: $Ri = \frac{N^2}{\mu^2} = \frac{gE}{\mu^2}$ where: *Vertical Shear:* $\mu = \left[\frac{\alpha V_z}{\alpha z} \right]^2$

Richardson Number: $Ri = N^2 =$ where: **Vertical Shear: $p = \frac{\alpha V_z}{\alpha z}$** ²

For a_z = vertical acceleration; g = acceleration due to gravity; z = vertical length; ρ = density;

S = salinity; t = temperature at ambient pressure; θ = potential temperature; V_z = vertical velocity.

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