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PROGRESSIVE VENTILATION OF THE OCEANS -  
POTENTIAL FOR RETURN TO ANOXIC CONDITIONS  
IN THE POST-PALEOZOIC

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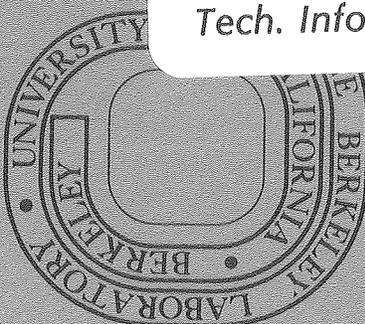
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PROGRESSIVE VENTILATION OF THE OCEANS -  
POTENTIAL FOR RETURN TO ANOXIC CONDITIONS  
IN THE POST-PALEOZOIC

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## ABSTRACT

After the ventilation of the residual anoxic layer in the late Paleozoic (Berry and Wilde, 1978) a return to ephemeral anoxic conditions in the ocean is suggested by anoxic sediments found in the Mesozoic cores of the deep-sea drilling program (Schlanger and Jenkyns 1977, and Theide and Van Andel 1977). A preliminary physical oceanographic model is presented to explain the development of oxygen depleted layers in mid-waters below the surface wind-mixed layer during non-glacial climates. The model shows the range of temperature, salinity and density values for hypothetical water masses for two climatically related oceanographic situations: Case A where bottom waters are formed at mid-latitudes at the surface salinity maxima, and Case B where bottom waters are produced at high latitudes but not by sea-ice formation as in the modern ocean. The hypothetical water masses are characterized by examples from the modern ocean and extrapolation to non-glacial times is made by eliminating water masses produced by or influenced by sea-ice formation in modern glacial times. The state of oxidation is made by plotting the model water masses on a oxygen saturation diagram and comparing the relative oxygen capacity with modern conditions of zonal organic productivity. The model indicates for Case A (high latitude temperatures above 5°C) two oxygen, depleted layers in the equatorial regions (1) from about 200m to the depth of completed oxidation of surface material separated by an oxygenated zone to (2) a deep depleted zone along the base of the pycnocline at 2900 M. The deep depleted zone extend along the Case A pycnocline polarward toward the high latitude productivity maximum. For case B with a pycnocline at about 1500m the deep anoxic layer is not sustained. Considerations of density only, suggest that neutral stratification and the potential for overturn is enhanced for climates transitional between Case A and Case B where the density contrast between major water masses formed at high latitudes and mid-latitudes is minimal or non-existent.

## INTRODUCTION

Berry and Wilde (1978) noted that dark (commonly black), organic-rich shales and mudstones are in relatively greater amount and spread more widely geographically in the Lower Paleozoic stratigraphic record than they are in the rock record of younger geologic intervals. They (Berry and Wilde, 1978) suggested that this relationship might be explained by a model of progressive oceanic ventilation. As Berry and Wilde (1978) noted, the origin and development of life and the related formation of an oxygen-rich atmosphere as discussed by Cloud (1976) implies that the early earth's ocean was anoxic. The stratigraphic record of Lower Paleozoic shelly fossil bearing, shelf sea rock sequences that contrast so sharply with coeval black, organic rich graptolite-bearing shales and the reduction in the extensive aspect of the dark, organic rich rock suites in the latter part of the Paleozoic suggests that oxygen was gradually and progressively mixed into the oceans, thus ventilating them. As soon as oxygen was present in the atmosphere, as it appears to have been through a significant part of the Precambrian (Cloud, 1976); oxygen would have been stirred into the

surface waters of the oceans through wind mixing. Wind mixing of oxygen into the ocean surface waters doubtless resulted in a ventilated upper or mixed layer of the ocean. Ventilation of the deep ocean waters, reasoning by analogy with processes active today, would have resulted primarily from the formation of cold, oxygen rich waters at high latitudes during periods of glaciation or at least sea-ice formation there. Such waters would sink and spread equatorward through the deep oceans. Sustained sinking of cold, oxygen-laden waters at cold polar areas would gradually ventilate the deep oceans, then, by advective upward mixing, progressively ventilate those mid-waters lying between the mixed layer and the deep waters. Anoxic mid-ocean waters would be ventilated from below. The decay of organisms that lived in surface or near-surface waters as they sink through the mixed layer would work against complete ventilation of such a residual body of anoxic water. Highly productive surface waters would yield large amounts of organic matter that would, in essence, consume, a large proportion of available oxygen during decay and so produce a body of oxygen minimum water, as is seen in modern oceans (Wyrski, 1962). Thus, particularly in areas of high surface water productivity, a body of mid-water that had been a part of the last water to be ventilated could become low in oxygen content and, perhaps even anoxic.

Berry and Wilde (1978) drew particular attention to the ventilating potential of cold waters with large quantities of oxygen that formed at glaciated or ice-bound polar areas. To that initial consideration of ocean ventilation may be added another mechanism for ocean ventilation. Relatively warm but salty waters formed under conditions similar to those in the present-day Mediterranean or Sargasso Sea where evaporation exceeds precipitation could result in denser, oxygenated waters that sink to and mix at some density equilibrium depth in the oceans. During past geologic times when warm, equable climates were widespread and oceanic circulation was sluggish, the prolonged existence of waters with large oceanic surfaces where evaporation exceeds precipitation could result in formation of relatively salty and oxygenated waters that sank to become deep or bottom water in the absence of cold high latitude deep water. Such areas where evaporation exceeds precipitation would be centered approximately at 30 degrees North and South latitude in the major desert areas.

Potentially, a certain degree of ocean ventilation could have taken place through salinity driven sinking. Broad shelf seas in areas in which evaporation was greater than precipitation could have been sites of formation of dense, salty water at the surface which would have sunk to become deep to bottom water and so facilitated life on or near the bottom in areas that had previously been anoxic. Some potential influences of mixing cold, polar waters and dense, warm relatively salty water is presented in model form herein.

The influences of high productivity over shelves and in upwelling areas was not brought into consideration in the initial discussion of progressive ocean ventilation (Berry and Wilde, 1978). Not only upwelling waters but also shelf seas are areas of high plankton productivity (Ryther, 1969). Highly productive surface and near-surface waters may lead to development of oxygen-poor waters at depth in areas where the

plankton decay while sinking. Potentially, such oxygen-poor waters may become anoxic if productivity remains high for a long interval of time and oxygen replenishment is slowed as a consequence of slow to no ventilation from below.

#### THE STRATIGRAPHIC RECORD

Dark (commonly black) organic rich shales are a common Lower Paleozoic rock suite (Berry and Wilde, 1978). Black graptolite or agnostid or olenid trilobite bearing shales that formed in basinal, slope, and even platform or shelf environments are recorded in stratigraphic sequences of Cambrian, Ordovician, Silurian, and Devonian age from many parts of the world. The rocks commonly are thinly laminated, contain pyrite seams and lenses, bear remains of planktic and nektic (but not benthic) organisms, and may contain unusually high concentrations of uranium and vanadium (Pettijohn, 1975). Certain of these shales have been mined for uranium (Martinsson, 1974).

Summaries of Cambrian stratal sequences in North America (Holland, 1971; Stewart and Poole; 1974) and Europe (Cowie, 1974; Leggett, 1980; Martinsson, 1974; Rushton, 1974) suggest that dark, organic rich shales and mudstones are the most common rock suite formed in outer shelf and slope as well as basinal environments in the latter part of the Cambrian. Cook and Taylor (1977) described a Late Cambrian shelf to basin depositional environment transition in Nevada, depicting thinly laminated black lime mudstones typical of the slope deposits and slide and flow deposits of shelf origin that are interbedded with the hemipelagic slope and basin sequences. Dark shales do not appear to be markedly widespread in rock sequences of Early and early Middle Cambrian age, suggesting that not until the late Middle and Late Cambrian did anoxic waters spread widely across the outer margins of shelves and their slopes. Harland (1974) and Cowie (1974) drew attention to a relatively long glaciation (the Varangian) in the Late Precambrian. Harland (1974, p. 29) noted that the Varangian glaciation was "severe and prolonged" and that evidence of it may be seen in Greenland, Scandinavia, northern Scotland, and Australia. The Varangian glaciation potentially could have ventilated the world's oceans. That it permanently did not is indicated by the widespread black shales of Late Cambrian and younger ages in the Paleozoic.

Areas influenced by Varangian glaciation in Scotland, Greenland, Scandinavia, and Australia appear to have been in the Tropics by the Late Cambrian because thick and extensive limestones of that and younger Paleozoic ages occur there.

The Late Cambrian black shales such as the Alum Shale in Scandinavia appear to reflect the culmination of a prolonged marine transgression across lands exposed during Varangian glaciation (Martinsson, 1974). The organic rich, and locally, petroliferous character of these shales suggests that organic productivity in the surface waters was high. As Leggett (1980) pointed out, the most likely planktic photosynthetic organisms in the Early Paleozoic were algae. Many taxa of green algae without shells are among prominent phytoplankton in modern seas. Similar organisms could have been present in Paleozoic oceans.

The widespread character of dark, organic rich shales developed in the Late Cambrian persisted into the early part of the Ordovician. Indeed, Early Ordovician was a time of wide development of black shales and lime mudstones across the outer parts of shelves as well as slopes and basins. Globally, by the latter part of the Ordovician, the widespread occurrence the dark, organic rich shales (or the graptolite biofacies) diminished (Berry and Wilde, 1978). This was in part a reflection of development of land areas in Africa and South America (Berry, 1974; Dean, 1980).

The stratigraphic record in Northern Africa and parts of South American indicate that an extensive glaciation occurred in those areas during the Late Ordovician. Isotopic age determination for Late Ordovician strata (Compston, 1979) indicate that this glaciation might have lasted for as long as 30 to 35 million years. The stratigraphic record in North Africa (Beuf and others, 1971) suggests that glaciation waxed and waned periodically during this glacial interval.

Dark, organic rich shales and lime mudstones that comprise the classic graptolitic biofacies are widely found in rock sequences of Early Silurian age (Berry and Boucot, 1968). Shelf areas were once again inundated progressively during widespread transgressions that followed after the Late Ordovician glacial interval and related draining of most shelf areas (Berry and Boucot, 1973). Anoxic waters again spread widely across outer margins of shelves as well as slopes and ocean basins (Berry and Boucot, 1968; Berry and Wilde, 1978). From about mid-Silurian (about the early part of the Wenlock) onward throughout the Silurian and continuing into the Early Devonian, anoxic waters apparently persisted along the outer margins of some shelves and along shelf slopes. The dark shales were not so widespread across shelves as earlier in the Silurian. By this time, oceanic mid-waters may have been ventilated to minimal anoxicity because the graptolite-bearing strata in north-central Wales of this age are not the typical black, organic rich graptolite shales. They are, however, thinly laminated and bear no traces of bioturbation (Watkins and Berry, 1977). They may have formed under low levels of oxygen content in the bottom water (Watkins and Berry, 1977). The Early Silurian stratigraphic record, is similar to that of the Late Cambrian and Early Ordovician in indicating that the most widespread development of black shales occurred during marine transgressions across shelf areas. Organic rich shales and mudstones that border thick carbonate sequences that formed in shallow shelf environments at times of marked transgression are notably more widespread than in regressive conditions.

Review and summary of Devonian worldwide paleogeography (Heckel and Witzke, 1979) and Devonian dark shales (Krebs, 1979) indicates that dark, organic rich shales accumulated on certain shelf margins and marine basins during the Devonian. Krebs (1979) pointed to a number of relatively short duration incursions of dark "basinal facies" shales across shelf sea environments in western Europe during the Devonian. Late Devonian dark, organic rich shales occur widely in eastern North America. Certain of these shales appear to have formed in relatively deep shelf environments on slopes in front of outbuilding deltas (Glaeser, 1979). Deep shelf and slope environments appear to have been

sites over which anoxic waters formed in the Devonian, but the worldwide areal spread of these sites appears to have been less than at earlier times.

Faunal and stratigraphic records of the Late Paleozoic (C.A. Ross, 1979; J.R.P. Ross, 1979; Olson, 1979) and Mesozoic ocean basin sediments (Bernouilliand Jenkyns, 1974; Jenkyns, 1978, 1980) suggest that the oceans were ventilated by the Late Paleozoic and remained so, apparently as a consequence of Late Paleozoic glaciations that occurred in the present-day southern hemisphere continents. Shelf seas were relatively limited in extent during the Late Paleozoic and Early Mesozoic, though Haekel (1977) suggested that certain Pennsylvanian black shales in the mid-continent of North American could have formed under anoxic shelf sea waters that were transgressive.

Return of widespread shelf sea conditions for intervals of the Mesozoic appear to have resulted in the Cretaceous Anoxic Events (Arthur and Schlanger, Schlanger and Jenkyns, 1979; Thiede and Van Andel, 1977). In these and perhaps certain Jurassic (Hallam, 1975; Jenkyns, 1980) intervals, oxygen-poor mid waters appear to have become anoxic and to have spread across outer parts of shelves and upper parts of slopes. Perhaps the Cenozoic Monterey Shale and related organic rich shales in California and similar deposits in Chile and Japan (Garrison, 1975) are reflective of similar changes in the oxygen minimum zone for limited intervals of time. Arthur (1979) gives a summary of the Cretaceous to modern situation.

#### THE MODEL

Berry and Wilde (1978) proposed a model for the progressive ventilation of the ocean from its initial anoxic state before the evolution of oxygen producing organisms to its present well oxygenated condition (Appendix A). The two primary ventilating processes proposed were (1) wind induced mixing of the surface layer of the ocean and (2) sinking of cold oxygenated waters formed at high latitudes accompanying sea ice formation during glacial times. In the present ocean, essentially glacial times with permanent ice at high latitudes, the major factor in forming water masses is the wide variation in temperature as the variation in open ocean salinity is small. Accordingly, the majority of the ocean is cold and well oxygenated reflecting the high latitude origin of deep and bottom waters. Salinity induced sinking of major water masses occurs today only at mid-latitudes where evaporation exceeds precipitation. Mediterranean water in the Atlantic and Red Sea water in the Indian Ocean typify the result of evaporation in these marginal seas and in central waters of the world's oceans forming polarward of the open ocean salinity maximum at about 20° latitude. The volumes involved in such water masses are relatively small and surficial compared to the volumes of temperature induced sinking.

However, in non-glacial times with a more moderate climate and much less thermal contrast between the equator and the poles, salinity driven density contrasts at mid-latitudes may produce significant water masses in mid to even deep and bottom waters. As it is difficult or impossible to know the actual temperature and the evapro-precipitation ratios

during non-glacial periods, it seems appropriate to model such changes as a continuum and define the conditions governing which combinations of temperature and salinity are producing the major water masses. A way to illustrate the interrelationship of temperature and salinity on density is the Helland-Hansen (1916) diagram in which temperature and salinity are plotted linearly with density contoured on the plot. Density is given as Sigma-T

$$\text{Sigma-T} = (\rho - 1) \times 1000 \quad (1)$$

where

$$\rho = \text{Density in gms/m}^3$$

and

$$\text{Sigma-t} = f(\text{Temperature and Salinity})$$

(Cox, McCartney, and Culkin, 1970).

Figure 1 shows such a diagram for hypothetical limits of water mass formation for two climates in non-glacial times:

Case-A Maximum non-glacial conditions with minimum thermal contrast between equatorial and polar regions;

Case-B transition conditions either leading to or coming from glacial conditions, but without significant sea ice formation.

The assumptions for these diagrams are:

- (1) The range of salinity variations and the mean salinity of the ocean has been essentially constant since early in the Paleozoic, as the fossil record indicates that certain marine stenohaline organisms such as crinoids, brittle stars, and starfish have survived with little change morphologically, and, apparently, in modes of life since the early Paleozoic.
- (2) Wust(1936) calculated an empirical relationship between evaporation and precipitation which results in surface salinities. That relationship obtains since the Precambrian or:

$$\text{Surface Salinity (}^\circ\text{/}^\circ\text{)} = 34.60 + 0.0175 (E-P) \quad (2)$$

where

E-P = Evaporation-Precipitation in centimeters.

This gives a mean salinity of 34.6‰ sufficiently close to the modern mean of 34.72 ‰(Montgomery, 1958, p.146)

- (3) The maximum precipitation belts will always be equatorial and at high latitudes so that the minimum salinity by EQ(2) will be 33.75 ‰ using an Equatorial E-P=-60m (Wust, 1936). This defines a left hand boundary to Figures 1 and 2. This boundary may shift right to higher salinities with decreasing temperatures as cooler air has less moisture capacity than warmer air.
- (4) Non glacial times are defined by no or negligible sea ice formation. The minimum temperatures would be above the freezing point of sea water or:

$$FP (^{\circ}C) = 0.036 - 0.0499 \text{ SAL } (^{\circ}/_{\infty}) - 0.0001125 \text{ SAL } ^2 \quad (3)$$

- (Fujino, Lewis, and Perkin, 1974, p. 1797). For 33.75 ‰ the freezing point is about -1.8°C.
- (5) Due to the bi-modal distribution of maximum surface salinity between the minimum salinities at the Equator and high latitudes, the maximum temperature at a given salinity would lie on a line (Fig. 1) from maximum precipitation conditions at the Equator, (Equatorial Water (EQW)), to the surface salinity maximum area where salinity maximum water (SMW) is formed. This line would represent changes in latitude from 0° to about 40° in the Modern Ocean, or to the right of EQW (Fig. 1). Polarward of salinity maximum water mass formation (to the left of SMW) precipitation increases. For the model, the high latitude maximum precipitation region begins at 13°C which is the warmest high latitude average temperature for the modern zone 40°-50° latitude (Sverdrup et al, 1942, p. 127). Based on modern formation of high salinity 18°C water (Worthington, 1959), high latitude water (HLW) could form at any temperature below 18°C. The real value during non-glacial times would depend on the latitudinal (E-P) gradient.
- (6) For volume considerations, the mixing of high salinity and low salinity waters are considered to produce ocean water of mean salinity to comply with assumption (2).
- (7) The hypsographic curve (Kossinna, 1921, Menard and Smith, 1966) showing the distribution of depths in the ocean is effectively unchanged at the world wide scale, since the beginning of the Paleozoic.

#### CASE A

#### WATER MASSES

Figure 1 gives the model T-S diagram for non-glacial conditions. To separate the environmental conditions of Case A from Case B, which is transitional to and from glacial conditions, we will define normal Case A times as having a thermal contrast and evapro-precipitation gradient so that salinity maximum water (SMW) is a denser than high latitude water (HLW). This does not preclude denser shelf sea water but speaks

only to the major oceanic water masses. Figure 1 shows that using 18°C water as a model salinity maximum water (Worthington, 1959), all HLW must be formed at 5°C or warmer.

A longitudinal section Figure 2 shows the position of the water masses formed during these conditions. EQW would be the highest water spreading polarward from the Equator. SMW would be formed at the salinity maximum spreading both polarward and equatorward. SMW and EQW would spreading equatorward and mix to form subtropical water (STW) which would sink under EQW. SMW spreading polarward would cool and reach a maximum density at 18°C (By analogy with 18°C water of Worthington (1959). Some of the water would sink and maintain its identity as salinity maximum water (SMW). On the polarward margins the SMW would mix with HLW to form an intermediate water (IW) in which would sink to a depth above pure SMW. Under special circumstances the coldest HLW can mix with SMW to produce bottom water at high latitudes (SMBW). Shelf sea water (SSW) forming at mid-latitudes in the zone of maximum evaporation would mix and accelerate the sinking of SMDW. However, due to the much larger volumes of open ocean water masses, the SSW likely would lose its identity as does Meditterrean and Red Sea Water in the Modern Ocean. By analogy Figure 1 shows that mixing of 18°C (SMW) with Mediterranean Water (MW), a typical example of SSW, would produce denser water than SMBW for a ratio of SMW:MW less than 9 to 1.

#### OXYGEN CONDITIONS

Figure 3 shows the Model T-S Pattern plotted with oxygen content contoured instead of density. Due to the strong inverse relationship between oxygen solubility and temperature (Weiss, 1977) the high latitude waters have appreciably higher initial oxygen content than low to mid latitude waters. For modern conditions, oxygen consumption for 18°C water, which sinks only to 400 meters, is 0.5 ml/l/year (Worthington, 1959, p.30). This indicates for an initial oxygen content of 5.35 ml/l, recycling to the surface or contact with another source of oxygen must be within 10 years. 18°C water presently occurs in the upper ocean where oxygen consumption is highest due to surface produced organic oxygen demand. However Munk (1966, p. 716) estimates that oxygen consumption in the deep ocean ranges from 0.0027 to 0.0053(ml/l)/year. For the mild climate of Case A, the minimum cycling times are given in Table I. The actual rate of consumption with depth is described by Wrytki(1962) as

$$R = R_0 e^{-\alpha Z} \quad (4)$$

where:

R = Rate of consumption at depth Z

$R_0$  = Surface consumption which is  
a function of local productivity

$\alpha$  = attenuation co-efficient related to properties  
of oxidizable substances available

Z = depth.

However for this model the mean values as noted will be used in lieu of the precise values needed to solve EQ(4).

TABLE 1 OXYGEN CONDITION

Water Mass	Maximum Initial O <sub>2</sub> Content ml/l	Cycling Time Before Depletion	
		Years <sup>1</sup>	Years <sup>2</sup>
Equatorial Water(EQW)	4.5-4.8	1125-1200	9
Salinity Maximum Water (SMW)	5.1-5.35	1275-1338	10
Intermediate Water (IW)			
At Average Salinity	5.8-6.3	1450-1575	10.2-12.6
Central Bottom Water (CBW)			
At Average Salinity	6.3-6.5	1575-1625	
High Latitude Water (HLW)			
At 13 °C	6.0	1500	
At 5 °C	7.2	1800	
At -2 °C	8.4	2100	
High Latitude Deep Water	6.5-8.4	1625-2100	

1:Oxygen Consumption: Mean Value of .004(ml/l)Year  
 Deep Ocean Range .0027 to 0.0053(ml/l)Year  
 (Munk 1966,p.716)

2:Oxygen Consumption: .5(ml/l)Year (Worthington, 1959,p.302)  
 Surface

## CASE B

### WATER MASSES

As noted above, Case B is indicative of transitional conditions entering or leaving glacial times. That is, high thermal contrast, but without significant sea ice formation. Figure 1 gives the proposed T-S relationships and Figure 4 shows the Longitudinal distribution of the water masses. The major difference is the addition of water mass formation below  $5^{\circ}\text{C}$  with bottom and deep water formed at high Latitudes rather than from salinity maximum water at the mid-Latitude. The modern analogy for this low salinity and temperature water is Antarctic Intermediate water (Sverdrup et al, 1942, p.619). The latitude of temperatures from  $13^{\circ}\text{C}$  to  $5^{\circ}\text{C}$  shift Equatorward so that waters called HLW<sup>a</sup> in Case A are on a continuum to colder high latitude waters. HLW<sup>a</sup> is reserved for low salinity waters from  $5^{\circ}\text{C}$  to  $-2^{\circ}\text{C}$ .

Then sinking of HLW<sup>b</sup> to form deep and bottom waters also converts the salinity maximum bottom water (SMBW) of Case A to a new intermediate water. To avoid confusion the old designation SMBW is maintained although it is no longer the densest water mass. Conditions above  $5^{\circ}\text{C}$  would be the same as Case A except for an Equatorward shift. However, it seems likely that the major water mass formation would shift to the lower temperature regions of HLW<sup>b</sup>, as the greater density would indicate a higher rate of formation. With extended cold temperature regions of water formation SMW cannot mix directly with the new HLW<sup>b</sup>, as SMBW intervenes. Accordingly, HLDW would be a mixture of SMBW and HLW<sup>b</sup>. The mixing line between  $18^{\circ}\text{C}$  SMW and  $5^{\circ}\text{C}$  HLW<sup>b</sup> would be analogous to the central water of the Modern Ocean. The maximum open ocean density increases to 27.2 Sigma-T so that the mixing ratio for SMW/SSW as typified by MW is now about 3:2 making it even less likely that SSW could penetrate to deep depths before losing its characteristics by mixing.

### OXYGEN CONDITIONS

Figure 3 shows the additional oxygen capacity of HLW<sup>b</sup> compared to Case A conditions. With the confinement of Case A waters to shallower depths by the sinking of colder high latitude water, the chances for cycling back to the surface or contact with the wind mixed layer are enhanced.

### VOLUMES

The amount of water of given characteristics for the specified climatic conditions is a function of the rate of formation, the area of formation, and the residence time of the water mass in the ocean. A maximum value for modern rates of formation is given by Munk (1966) caused by the freezing of the Antarctic ice pack as  $9 \times 10^{20}$  grams/year or  $9 \times 10^{17}$  liters/year. At this rate the entire volume of the ocean  $1.369 \times 10^{21}$  liters (Montgomery, 1958) could be supplied in about  $1.5 \times 10^3$  years. However, it is unlikely that sufficient data can be derived from the geologic record to calculate volumes in this direct manner.

Another method to estimate volumes is to use the assumption of

constant average salinity and to use the T-S plot to determine what mixing ratios (volumes) between water masses will maintain the average salinity of the ocean. Assume for non-glacial times the two major water masses are SMW (High Salinity) and HLW (Low Salinity), ignoring volumetrically EQW (Low Salinity) and SSW (High Salinity). Thus, the mixing ratio of SMW/HLW is .36 on 36% SMW formed to 64% HLW (Fig. 1).

The hypsographic curve (Kossina, 1921, and Menard and Smith, 1966) can be used to estimate the range of depths occupied by the water masses for Case A and B climates. The hypsographic curve is given as a function of area and depth so

$$V = \int A dz \quad (5)$$

where

V = Volume  
A = Surface Area  
Z = Depth

Integration of the hypsographic curve to give the oceanic volumes as a function of depth is given in Appendix B. Figure 5 shows the hypsographic curve for volume as well as for the conventional oceanic area, with the volumes of each major water mass plotted based on the T-S mixing ratios. The intersection of the volume % and the volume curve gives the depth to which that water mass as bottom water would fill the ocean basin. Replotting the depth ranges on the area hypometric curve (Figure 5) gives the bottom area intersected by the water masses. By analogy with modern conditions using a wind mixed surface layer of 200 meters, the base of the pycnocline would be 2900m for Case A and 1500m for Case B. These would be minimum depths as consideration of other water mass production would shift the base to deeper depths; although the ratio of SMW:HLW would still be 36:64.

#### GEOLOGIC IMPLICATIONS OF THE MODEL

The circulation models for Case A and B can be used to estimate the oxygen conditions with depth and latitude with the addition of information on the magnitude and distribution of organic matter in the ocean. As a first approximation, high productivity is found in zonal belts at the Equator and today at about 60° N and S at the areas of planetary upwellings. Minimum productivity is found at mid-latitudes at the planetary oceanic convergences at the approximate latitude of the salinity maxima.

For the climatic conditions of Case A, with the general lower oxygen saturation values, the ventilation of the ocean is the poorest. Fig. 6 shows the Case A longitudinal section with potential oxygen depleted depths shaded. The high production at the Equator would produce a shallow depleted zone below the mixed layer 200m to a depth at which the surface organic matter would be oxidized. A deeper depleted region would be found along the base of the Case A pycnocline with its origin in the productivity maxima at high latitudes. Because of the deep pycnocline of Case A, the residence time of the water sinking along

the pycnoclinal density is long so the water continues to be depleted in oxygen. There would be a mid pycnoclinal aerated zone below the Equatorial depleted zone and above the depleted layer at the base of the pycnocline as this water has its origin in the low productivity areas of mid-latitude and would have a low oxygen demand. Whether these zones would be anoxic is a function of the residence time of the water masses and contact with other oxygenated waters. For Case A, with its initial low oxygen saturation values compared to the Modern Ocean, it seems likely that the oxygen depleted areas indeed would be anoxic. Geologically, it would mean at the Equator a return to anoxic conditions below 200m seen in the Paleozoic and that the outer continental shelf and upper slope would be anoxic. A deep Equatorial anoxic zone explains the anoxic events of Schaller and Jenkyns (1977) and Thiede and Van Andel (1977) in the Cretaceous. As seen in Fig. 3 the maximum depletion would occur at the mildest climates and the lowest temperature contrast between the salinity maximum and high latitudes.

(For Case B Fig. 7), the oxygen depleted zone would follow the shallower base of the pycnocline. The two Equatorial depleted zones of Case A (Fig. 6) would merge for Case B. With the strong temperature relation between oxygen solubility and temperature, the lower temperatures of Case B indicate a lesser probability of actual anoxic conditions except in the Equatorial Belt.

#### STRATIFICATION AND POTENTIAL OVERTURN

In both Cases A and B the oceans are density stratified except for the condition for  $5^{\circ}\text{C}$  for high latitude water mass formation, where the density of HLW and SMW are the same. The stability factor (Defant, 1955, p. 195-201) is a function not only of the density distribution with depth, but also the compressibility and the adiabatic effect so that simple low density contrast in a deep ocean is not sufficient to initiate Benard type convection or overturn. However, the oceanic climatic boundary conditions between Case A and B certainly suggest potential neutral stability conditions. The possibility for periodic overturn of oxygen depleted mid-waters into the upper pycnocline and the mixed layer has interesting geologic and evolutionary implications. It is interesting to note such conditions occur with a reasonably large temperature contrast between  $18^{\circ}\text{C}$  for SMW and  $5^{\circ}\text{C}$  for HLW, rather than for small temperature contrast, as one intuitively would expect. This paradox is due to the conservation of the average salinity and the change in surface salinity related to the zonal change in evaporation minus precipitation.

The potential for overturn conditions would thus occur not only as a precursor of the onset or cessation of true glacial times (freezing of sea ice); but also during nonglacial times which are cooler than Case A conditions.

#### SUMMARY

As Jenkyns (1980) noted, the dark, organic rich shales appear to have been most widespread at times of marine transgression. The record of Late Cambrian, Ordovician, Silurian, and Devonian dark shales on

shelves of the time is fully consistent with maximum development of these shales at times of most extensive transgression across shelves of the time; notably, those that lay under warm temperate to tropical climates. The stratigraphic record also indicates that the greatest development of dark, organic rich shales was at a time when climates were mild and equable globally. Oceanic circulation would have been relatively sluggish at such times. Equable climates globally could have enhanced formation of relatively saline and dense water; such intervals in time would not have been those during which cold waters formed at the poles to any significant degree. Oceanic ventilation thus would have been limited during prolonged intervals of equable global climate and minimal ocean circulation. The Paleozoic dark, organic rich shales from, their lithofacies relationships and paleogeographic positions, seem to have developed primarily in areas in which (a) organic productivity in surface and near-surface waters was high, (b) in tropical to warm temperate conditions, and (c) at times of limited ocean circulation and equable climate. These conditions did not develop significantly in the Late Paleozoic and early part of the Mesozoic. When they did return at intervals during the Jurassic and Cretaceous, mid-water oxygen minimum zones became locally anoxic. Where anoxic waters impinged upon shelves or shelf slopes, dark, organic rich sediments accumulated.

Globally equable climates probably led to expansion of oxygen depleted waters and even to anoxicity in these waters not only as a consequence of relatively sluggish deep circulation, but also as a consequence of the expansion into deep oceans of warm waters with decreased oxygen-bearing potential. As the pycnocline expanded under globally equable climates, more of the ocean floor came under waters with minimal to no oxygen content. Global conditions that included mild climates and limited ocean circulation would lead the development of anoxic waters and the spread of such waters. High productivity in surface waters at times of mild climates would enhance the tendency toward development of an anoxic water zone or at least, to expansion of an oxygen depleted zone. The stratigraphic record of deep shelf and slope deposits formed during equable climatic conditions in the Cretaceous and Cenozoic is consistent with such a pattern of development of anoxic sediments.

Dark, organic rich sediments have great potential for being loci of accumulation of organic products leading to petroleum formation. (DOW, 1978) Indeed, many dark, organic rich mudstones and shales such as the Monterey Shale in California are petroleum source rocks. The apparent episodic development of anoxic sediments in the stratigraphic record and recognition of rocks formed at times of "anoxic events" may be of economic significance.

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Figure Captions:

Figure-1

Temperature/salinity/density  
Diagram showing proposed major water masses in non-glacial times  
Water mass abbreviations:

EQW = Equatorial water  
SSW = Shelf sea water  
STW = Sub-tropical water  
SMW = Salinity maximum water  
HWLa = High latitude water for Case A conditions  
HWLb = High latitude water for Case B conditions  
IW = Intermediate water  
SMBW = Salinity maximum bottom water  
MW = Mediterranean water

Figure-2 Longitudinal profile for Case A conditions. See Figure 1 for water mass designations.

Figure-3 Temperature/salinity/oxygen  
Saturation diagram with proposed major water masses in non-glacial times. See Figure 1 for water mass designations.

Figure-4 Longitude profile for Case A conditions with oxygen depleted zones shaded. See Figure 1 for water mass designations.

Figure-5 Hypsographic curves for volume and area of the world ocean-area data from Kossinna (1921). See Appendix B for volume calculations.

Figure-6 Longitudinal profile for Case A conditions with oxygen depleted zones shaded. See Figure 1 for water mass designations.

Figure-7 Longitudinal profile for Case B conditions with oxygen depleted zones shaded. See Figure 1 for water mass designations.

### DENSITY AS SIGMA-T

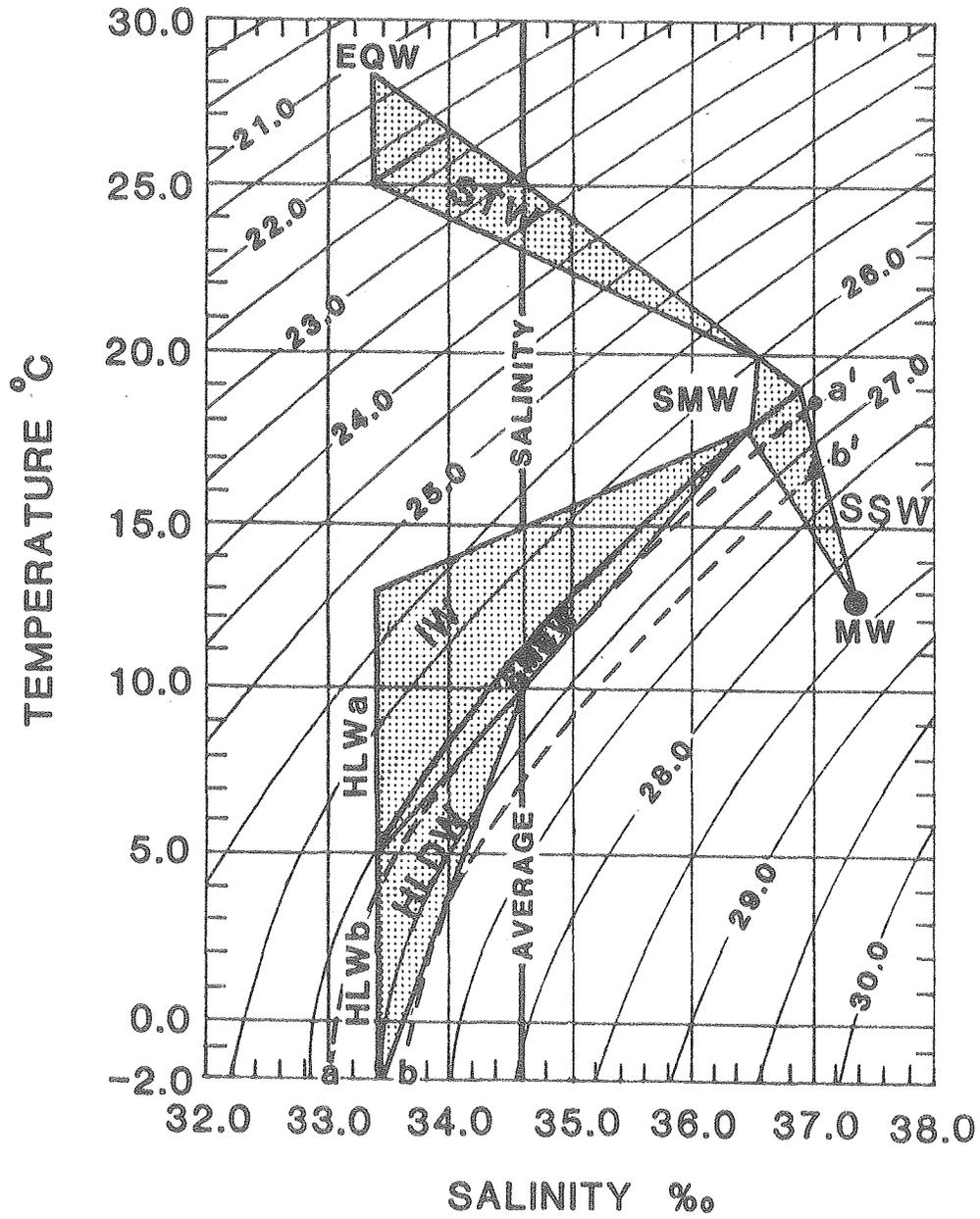


Figure 1

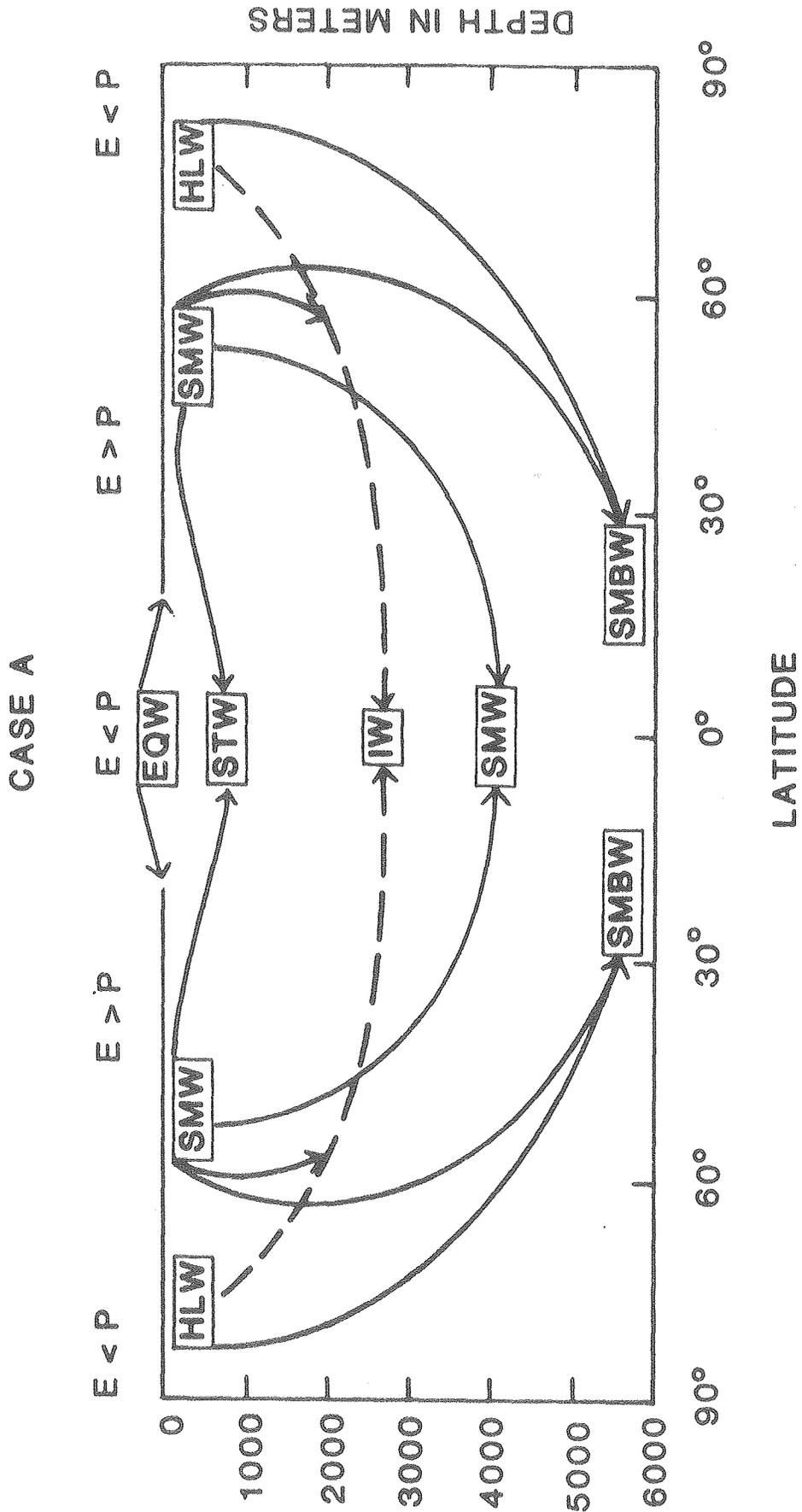


Figure 2

### OXYGEN SATURATION VALUES mL/L

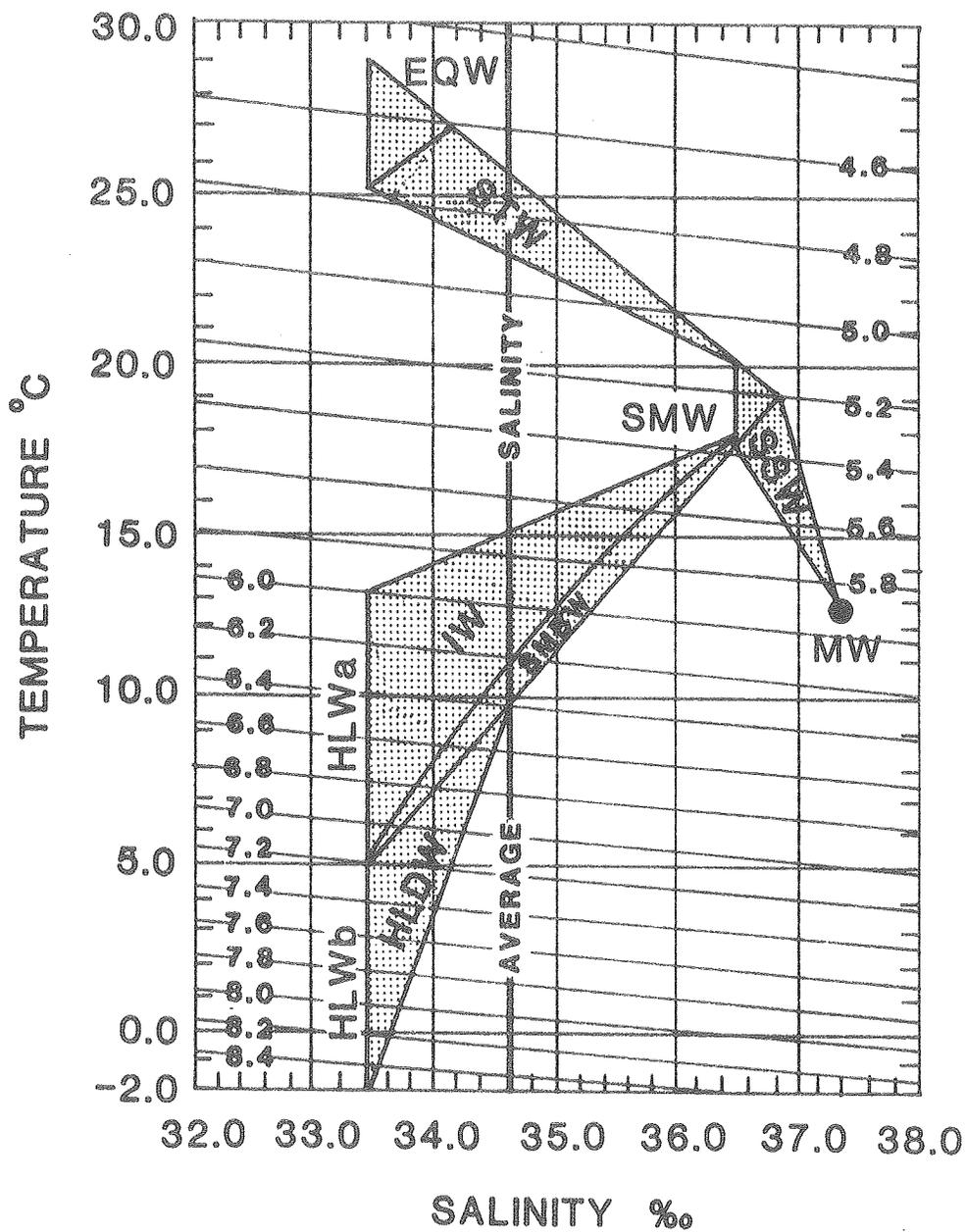


Figure 3

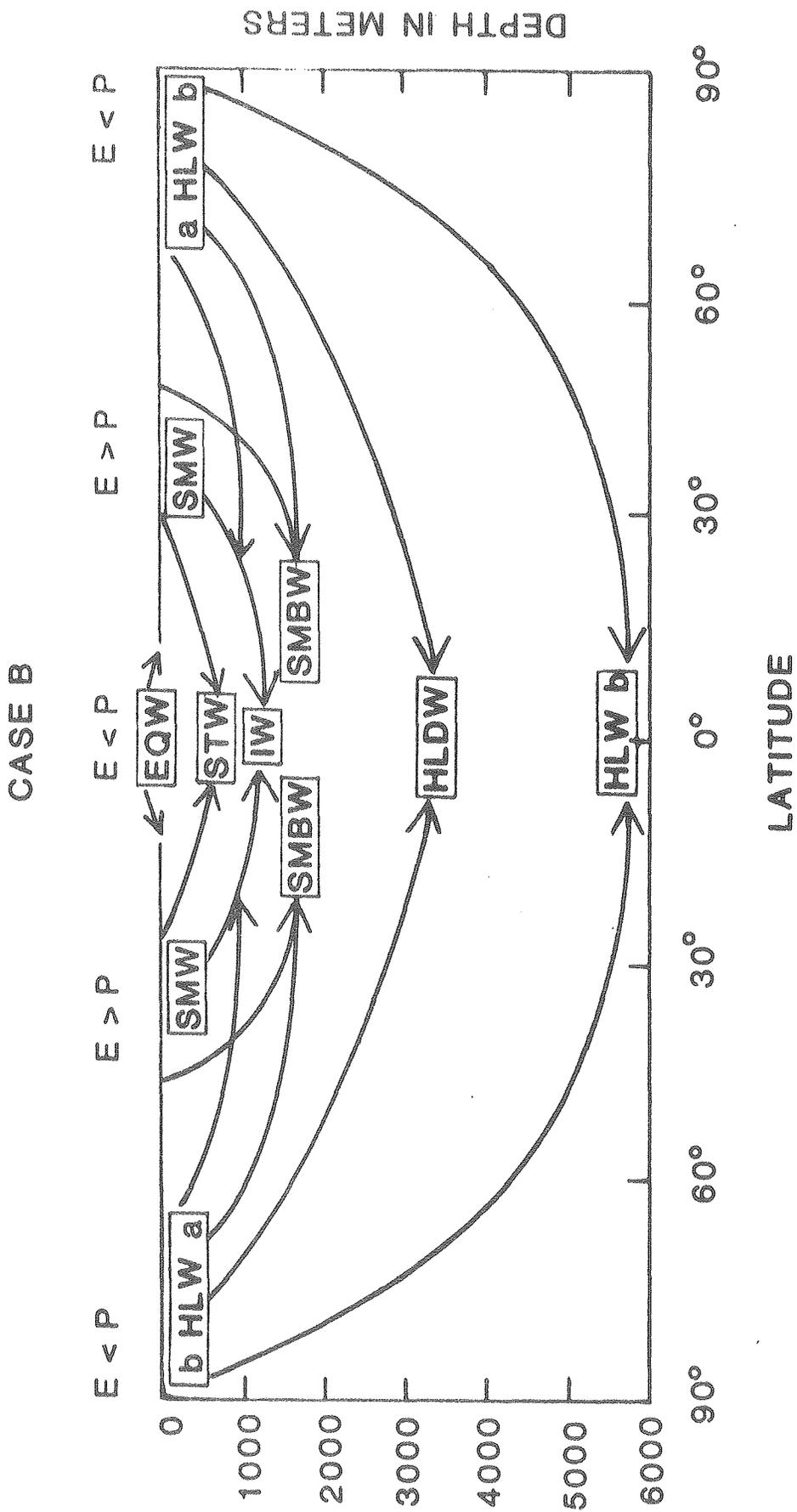


Figure 4

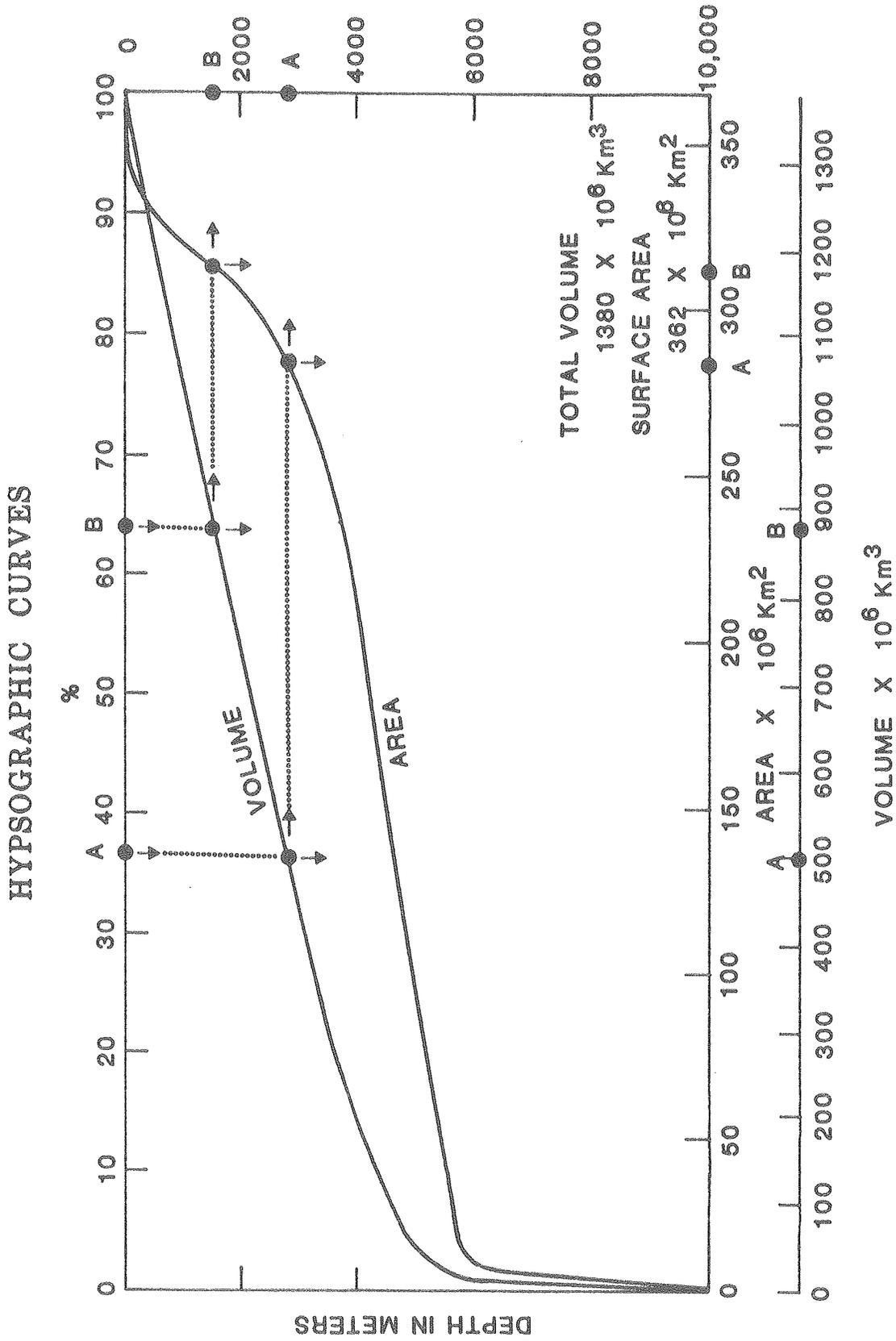


Figure 5

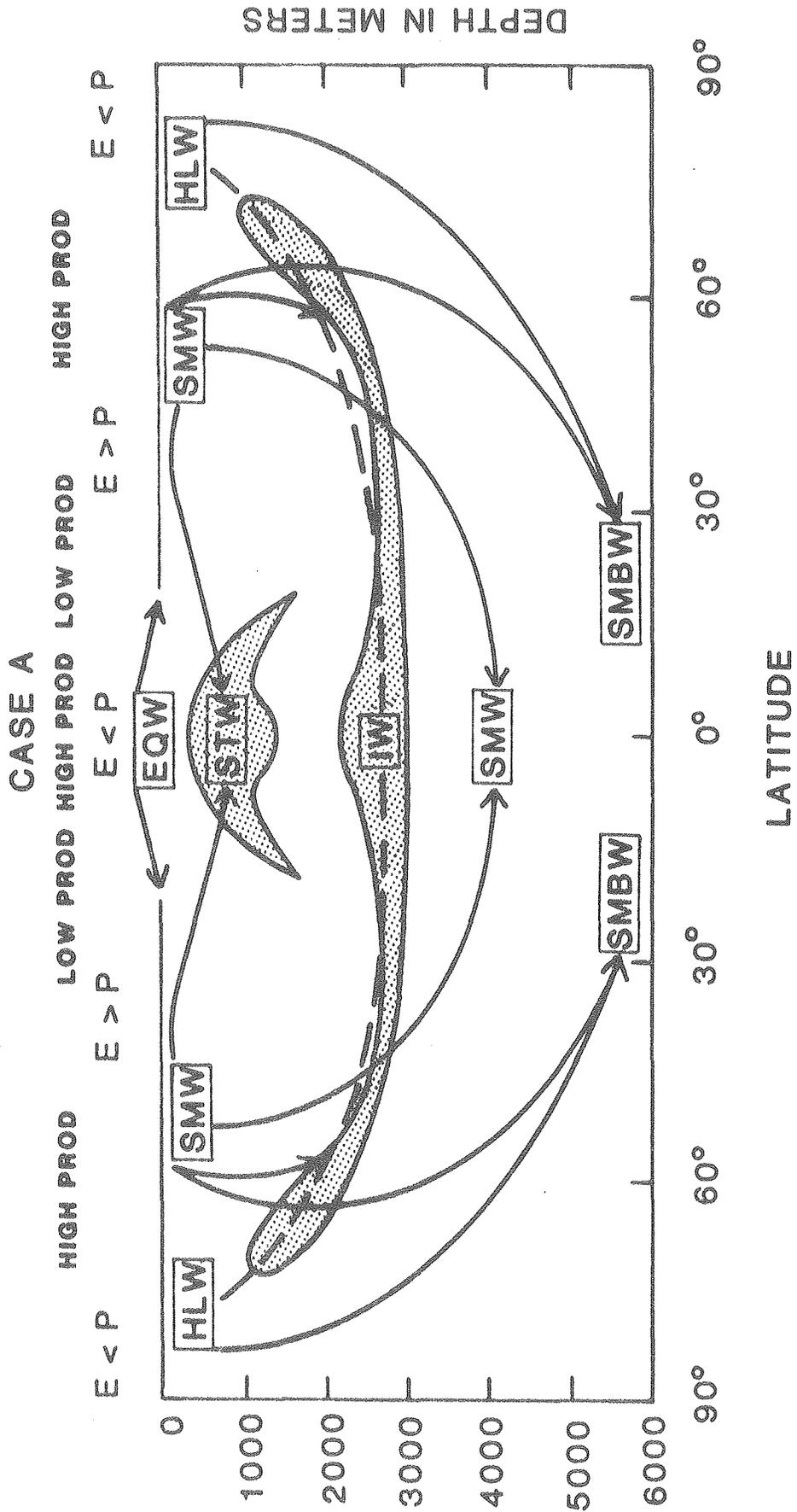


Figure 6

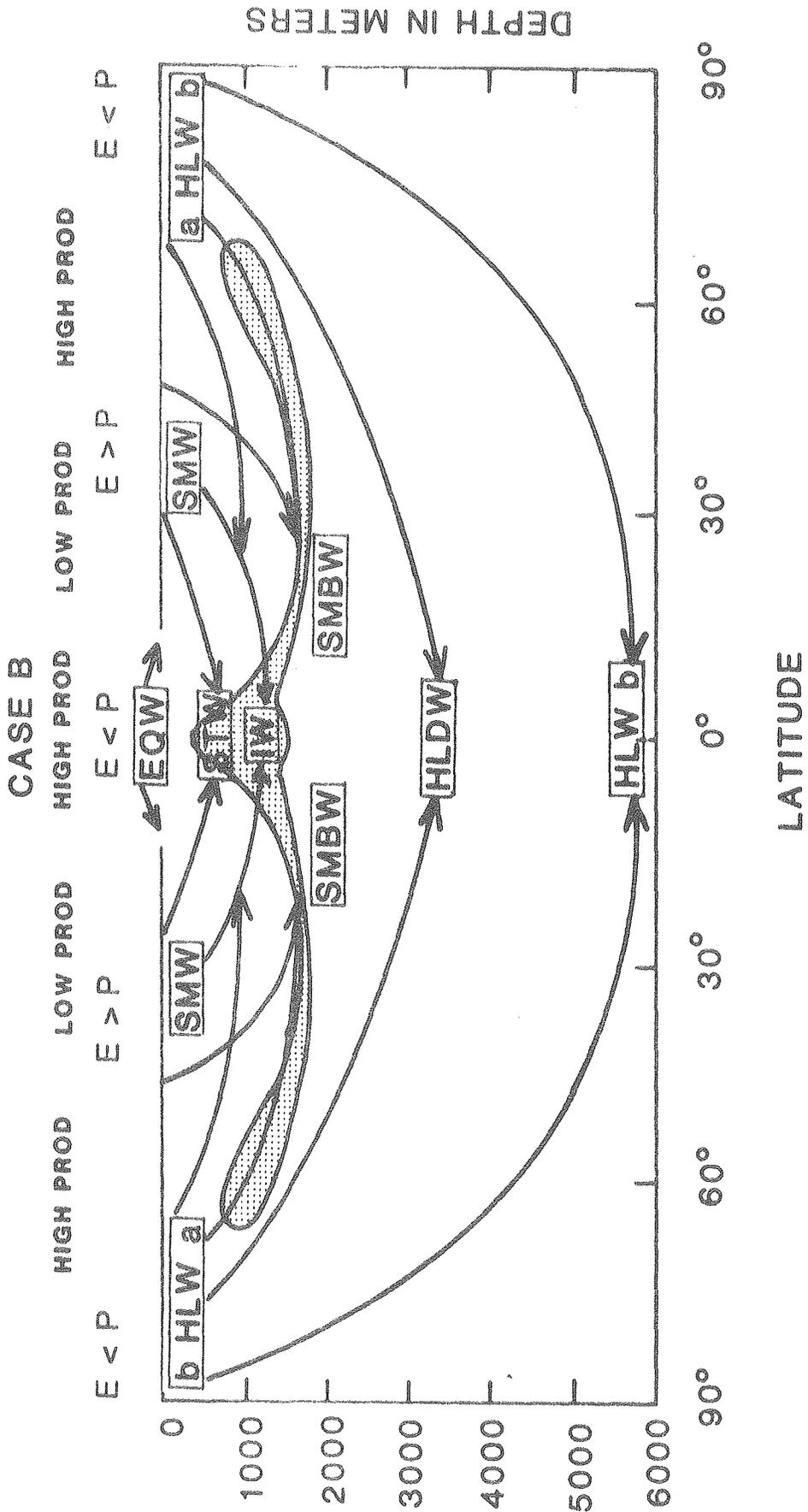


Figure 7

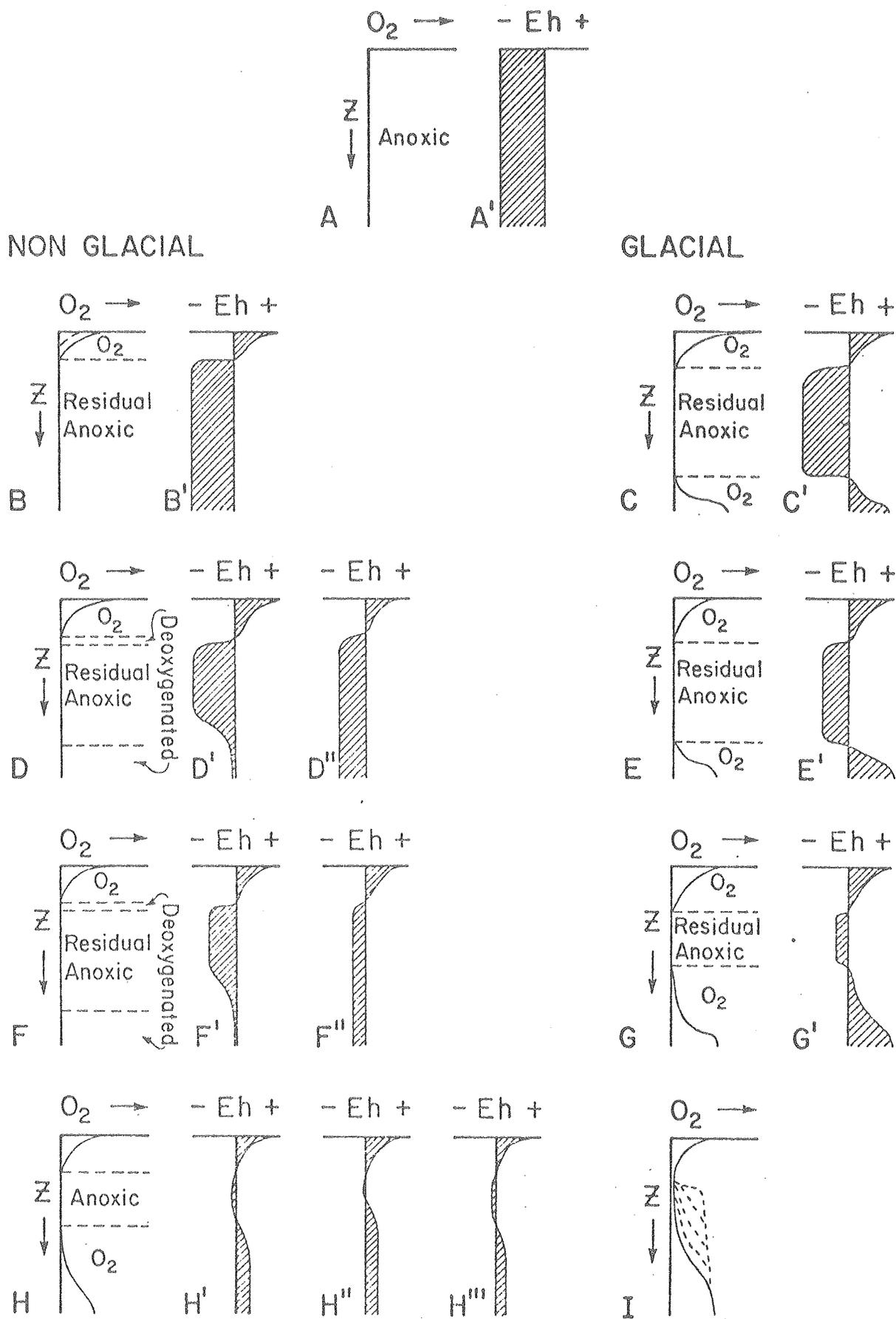


Figure 8

Appendix A

POSTULATED PROGRESSIVE VENTILATION OF THE OCEANS WITH TIME

(From Berry and Wilde, 1978)

The basic assumptions are: (1) initial anoxicity fixed at time A with only minor additions from organic rain; (2) atmosphere is the source of  $O_2$ ; (3) organic productivity effectively constant; (4) transfer of  $^2O_2$  in oceans by diffusion much slower than by wind mixing; (5) conditions depicted are for mid to lower latitudes; and (6) non-glacial episodes were much longer in duration than glacial. Z on the left of the diagrams is depth of water increasing downward.  $O_2$  expresses the oxygen content and increases to the right. Eh is the oxidation-reduction potential with the center line representing 0 Eh. Negative Eh is to left of the center line, and positive Eh is to the right. No absolute scale is intended and all values are relative. The diagrams express the following steps:

- (A) Pre-photosynthesis - no free oxygen in the atmosphere and Eh of oceans was at some maximum negative value;
- (B) Photosynthesis begins - non-glacial climate, depth of oxygen minimum increases as free oxygen is wind mixed into the surface ocean until some equilibrium profile values of  $O_2$  are reached as functions of effective wind stress, organic productivity, and oxygen solubility in sea water; the result is that the upper layer of the ocean is aerated with little effect on anoxic conditions of deep ocean;
- (C) Glaciation - depth of oxygen minimum (top of residual anoxic layer) increases as a result of increased effective wind stress and generally colder temperatures (with higher oxygen solubility); thermal contrast between the equator and high latitudes begins deep ventilation of the oceans with sea ice formation at high latitudes; total anoxicity is lowered;
- (D) Non-glacial interval - depth of oxygen minimum returns to depth in (B) as a result of milder climate; no ventilation of the deep ocean; deoxygenation occurs in deep water (D'); eventually, as a consequence of circulation, anoxicity is redistributed at some more positive value of Eh with time (D'); during mild climatic conditions, density stratification of the oceans would be less than during glacial times, hence oceanic conditions would be relatively more uniform;
- (E) glaciation - developments as in (C) except that as overall Eh goes up, ventilation is more effective relative to conditions in (C);
- (F) Non-glacial as in (D) - circulation increases overall Eh by consumption of oxygen from previously ventilated deep waters (F'');

- (G) Glaciation - developments as in (E); complete ventilation of the oceans is prevented by increased density stratification of the oceans with glaciation, thus preserving the residual anoxic layer at mid depths;
- (H) Non-glacial - redistribution of oxygen in deep waters essentially eradicates anoxic layer (H' to H''); with long duration of mild climate, anoxic waters below oxygen minimum may expand at mid depths, reflecting climatically mild environmental conditions as well as continued organic rain from surface (H'' ');
- (I) Glaciation - with anoxic layer initially small and Eh nearly positive, complete ventilation of the oceans may be achieved. Initially, overall Eh may be slightly positive. With subsequent glaciations, deep ocean values of oxygen increase to present condition of near-saturation as there is no effective oxygen demand below the oxygen minimum with continued deep ventilation. Conditions indicated in H'' may recur with long intervals without glaciation in areas of high productivity, and/or impaired circulation. Such conditions would have resulted in the Jurassic black shales described by Hallam (1975), the Cretaceous black shales cited by Berger and Von Rad (1972) in the Cretaceous, and the Mesozoic and Cenozoic black shales noted by Fischer and Arthur (in press). It is considered unlikely that the world-wide anoxic conditions would have persisted in the oceans after demise of the residual anoxic waters in the open ocean.

CAUTION: Although we hesitate to assign times to the above steps at this stage of development of the model, review and analysis of the Late Precambrian and Paleozoic rock and faunal record of glacial as well as non-glacial intervals suggest that: (1) glacial event (C) could have taken place in the Late Precambrian; (2) Glaciation (E) may have been in the Late Ordovician; and (3) Glaciation (G) might have occurred in the Middle Devonian. The glaciation labelled (I) could have taken place in the Late Paleozoic with the fluctuations indicated (H', H'', H' ") developing as a consequence of climatic conditions during the Mesozoic and Tertiary. The uppermost curve (dashed) in (I) could have developed as a consequence of the Pleistocene glaciation. The number of glacial/non-glacial cycles is not fixed. Theoretically, ventilation of the oceans could be accomplished in one extended glaciation. Formation of extensive sedimentary sequences under anoxic conditions as described in this paper suggests that ventilation proceeded in a step-like manner. This figure is intended as an initial working model which is, of course, subject to revision with additional geologic and oceanographic data.

Appendix B.

Volumetric Hypsographic Curve Calculations

For

$$v = \int dAdz$$

$\Delta$  volume =  $\Delta$  depth x average area

or

$$\begin{aligned} V_i - V_{i-1} &= (Z_i - Z_{i-1}) \cdot \left( \frac{A_i + A_{i-1}}{2} \right) \\ &= \Delta Z \left( A_{i-1} + \frac{\Delta A_i}{2} \right) \end{aligned}$$

let

$\Delta Z_i$  = interval from  $A_i$  to  $Z_{i-1}$

$$\Delta Z = Z - Z_{i-1}$$

then

$$\Delta V = \Delta Z \left( A_{i-1} + \frac{\Delta A_i}{2} \times \frac{\Delta Z}{\Delta Z_i} \right)$$

Appendix B (continued). Computations for Figure Hypsographic Curves. Data for Areas from Kossinna (1921).

Depth (meters)	Area*	%	Comm. Area*	Comm. % Area	Volume*	%	Comm. Volume*	Comm. % Volume
10,000	0	0	0	0	0	0	0	0
6,000	4.5	1.2	4.5	1.2	9	0.6	9	0.6
5,000	84	23.2	88.5	24.4	46.5	3.3	55.5	3.9
4,000	120	33.1	208.5	57.5	148.5	10.8	204.0	14.7
3,000	70	19.3	278.5	76.8	243.5	17.6	447.5	32.3
2,000	24.5	6.8	303	83.6	290.75	21.1	738.25	53.4
1,000	15	4.1	318	87.6	301.5	212.5	1049.75	75.9
200	15.5	4.3	333.5	92.0	260.6	18.9	1310.35	94.8
0	28.5	7.9	362	99.9	69.55	5.0	1379.9	99.8

\*Units: Area -  $10^6 \text{ km}^2$   
 Volume -  $10^6 \text{ km}^3$