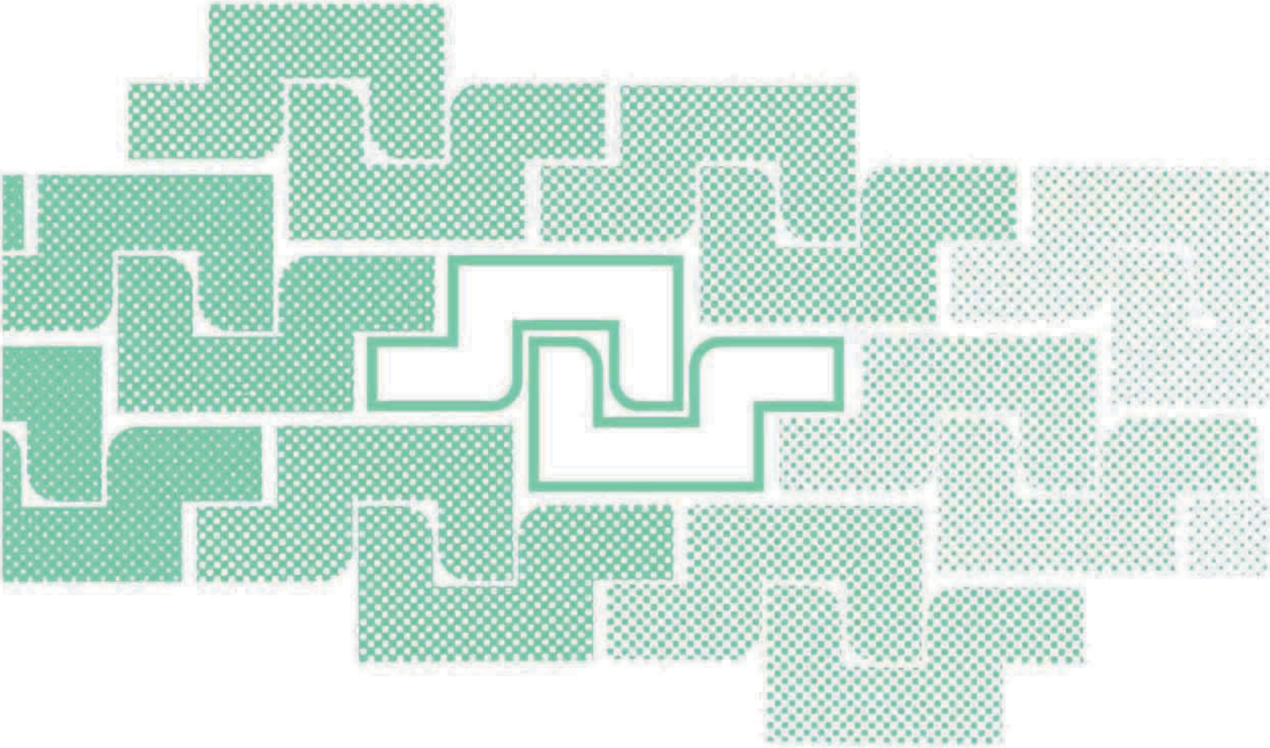

Past and Present Water Column Anoxia

Edited by

Lev N. Neretin

NATO Science Series

IV. Earth and Environmental Sciences – Vol. 64

Past and Present Water Column Anoxia

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Contents

Part III BIOGEOCHEMISTRY AND MICROBIOLOGY OF THE NITROGEN CYCLE

Part IV BIOGEOCHEMISTRY OF CARBON AND SULFUR CYCLES. MICROBIAL METAL REDUCTION

Part V MICROBIAL ECOLOGY OF THE OXIC/ANOXIC INTERFACE

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Foreword

Life on Earth emerged under anaerobic conditions. Many fundamental biochemical and metabolic pathways evolved before the atmosphere contained oxygen. Today, anaerobic (anoxic) conditions in marine milieus are generally restricted to sediments and to basins isolated from oxygenated deep-sea circulation. Oxygen-deficient or hypoxic conditions are defined in operational terms. In speaking of the degree of O_2-deficiency, the term hypoxic is usually defined as ranging between 22 and 64 μM of O_2, while suboxic refers to a range below 10 μM, and anoxic is the complete absence of oxygen. Biologists commonly use the term hypoxia to describe the point at which animals suffocate. But the papers presented in this book deal with the whole range of oxygen-deficient conditions, and the definitions some authors have used here may vary.

Enhanced oxygen consumption by decomposition of organic matter and slow downward mixing and diffusion of dissolved oxygen from the surface waters can lead to oxygen deficiency in the water column in highly productive waters, forming the Oxygen Minimum Zone (OMZ). Bottom waters of coastal upwelling regions are frequently exposed to hypoxic (suboxic) or anaerobic conditions owing to extremely high primary productivity. The development of these conditions represents an acute perturbation to ecological dynamics and fisheries. In the past, anoxic conditions in the water column may have developed more readily. Oceanic anoxic events (OAE) were episodes of globally enhanced organic carbon burial that significantly affected global climate by reducing atmospheric CO_2. An excess of nutrient loading leads to eutrophication of coastal areas and enclosed seas, a wide-spread global problem. The imbalance of nutrient cycles is often directly linked to increased urbanization in coastal river drainage areas or to increased agricultural activities in watersheds.

About 60 scientists gathered in Sevastopol, Ukraine, on the Black Sea coast for a NATO Advanced Research Workshop (NATO ARW) devoted to improving knowledge of pelagic anoxic environments. The workshop aimed to facilitate exchange and communication among scientific groups from the nine participating European countries, Chile, India, Japan, Jordan, the Russian Federation, Turkey, and the United States; and to define and set future research directions. The research specialties of participants ranged from hard rock geology and organic geochemistry, to mathematical modeling, and from microbiology and molecular biology, to biotechnology and bioremediation. The papers gathered in this volume reflect the interdisciplinary nature of the workshop and the complexity of the issues related to the formation and persistence of oxygen-deficient and anoxic conditions in the World Ocean though history. Not all chapters in this volume are based on presentations to the NATO ARW, however. This volume aims to bring together review-type papers by the most respected specialists in their fields, thus furthering discussion of the current state, and future directions, of research on pelagic suboxic and anoxic environments. The book is organized around several major topics such as (i) reconstructions of anoxic conditions during Earth's history, (ii) regional aspects of anoxia in the ocean and of eutrophication-induced hypoxia on the continental shelf, (iii) microbial ecology of the oxic/anoxic interface, (iv) the biogeochemistry of nitrogen and carbon, including methane cycling, and (v) the microbiology of the metal reduction. The studies presented here offer exceptional geographic coverage, including interdisciplinary research performed in almost all significant pelagic environments of the world ocean with permanent or transient anoxic conditions – such as the Black Sea, the Baltic Sea, the Cariaco Basin, the Arabian Sea, the Eastern South Pacific, Namibian upwelling area and others. Examples of human-induced hypoxia discussed in the book include seasonal oxygen deficiency over the north-western Black Sea shelf, the western continental shelf of India and in the Gulf of Mexico.

Multiple interdisciplinary approaches were obviously required to increase understanding of such systems. The combination of time-series studies with routine data collection, process studies on board larger ships, and new technologies (moorings, ARGO drifters, gliders and sensors) are advocated to improve our knowledge of temporal and spatial variability of anoxic environments. New data presented in the book highlight the importance of lateral ventilation processes in controlling the overall redox budget in many water column anoxic environments such as the Black Sea, the Cariaco Basin, and the Baltic Sea.

Nitrogen limits primary and secondary production in large parts of the ocean. Recent progress in the field suggests that the oceanic nitrogen cycle is more complex than we realized a few years ago. Existing global nitrogen budgets may be incorrect, because the rate of nitrogen loss was underestimated without considering the processes of anaerobic ammonium oxidation (anammox). Discovered first in a sewage plant, the anammox process appears to be widespread and important in natural environments. In view of the discovery of anammox, the observed deficit in the oceanic fixed nitrogen budget may be even larger. This suggests that either the oceanic nitrogen budget is far from being in a steady state, with a possible consequence for the CO_2 budget of the planet, or that oceanic nitrogen fixation is significantly underestimated. Our knowledge of nitrogen fixation under oxic and anoxic conditions, in particular in OMZs, is obviously insufficient.

The process of anoxygenic photosynthesis mediated by green sulfur bacteria is widespread in present anoxic marine environments, including the Black Sea. As confirmed by molecular methods, it was a common process in the past ocean. It is to a large extent responsible for sulfide oxidation in settings where light reaches the oxic/anoxic interface. Recent findings show that the green sulfur bacteria that dominated the Black Sea interface are unique with respect to their extreme light adaptation. Similar bacteria using other light wavelengths may survive in environments far below the zone of photosynthesis; for example, in hydrothermal vents. Therefore the use of the energy of light supporting life may be distributed in a broader range of environmental settings than we knew earlier.

The Black Sea is a natural biogeochemical laboratory for studying methane cycling. The key process regulating the flux of methane into the atmosphere is the process of methane oxidation that may happen anaerobically. New data suggest that the process of anaerobic methane oxidation does occur in the Black Sea water column. However, we are still far from constructing a concise methane budget for the Black Sea, and therefore, the role of anoxic systems in controlling the global methane inventory needs to be studied further. Methane and sulfur cycles in the water column in some upwelling areas, for example, are more closely linked with sedimentary processes of methane and sulfide production and oxidation as we previously thought.

Although the interpretation of records in extant anoxic systems provides a key to understanding their contemporary counterparts, limited understanding of present anoxic environments also affects the growth in our knowledge about the past. New molecular biological techniques such as fossil DNA profiling combined with lipid biomarker studies have proven to be a successful approach for reconstructing ancient sedimentary biogeochemistry and aquatic microbial communities. Sometimes the pool of molecular information that can be retrieved from ancient environments is called "Paleome". This is a new and exciting area of research, extending the frontiers of our understanding of the biosphere.

We hope that the enormous spatial and temporal complexity of pelagic anoxic systems on display in this book will stimulate new interdisciplinary thinking. As such it should be fully implemented in future research planning and stimulate the establishment of international, long-term, ecological programs for studying anoxic environments.

The Editor
Bremen, 17 August 2005

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I

MARINE ANOXIA DURING EARTH HISTORY

ANOXIA THROUGH TIME

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Abstract The rock record provides unequivocal evidence for multiple times in Earth history during which the entire global ocean or parts of it were characterized by severe oxygen-deficiency. Evidence includes geological and paleontological observations but also diverse geochemical fingerprints such as trace element abundances, organic geochemical markers or various isotope records, all of which are diagnostic for water column anoxia. The duration of such episodes of oxygen-deficiency ranges from a few thousand to millions of years. In fact, considering the proposed temporal sequence of oxygenation of the atmosphere-ocean system during Earth's early history with the ventilation of the deep ocean not earlier than 1 Ga ago, it appears that the modern oxic world represents an exceptional state of the atmosphere-ocean system on our planet during its 4.5 Ga years history.

Keywords: Oceanic anoxic events, proxy signals, earth system evolution

1. INTRODUCTION

Earth scientists, specifically those studying the low temperature sedimentary realm, define the term "anoxia" as an environmental situation in which the abundance of free molecular oxygen is at (or very near) zero. Thereby, the attribute "anoxic" is applied to all scales, ranging from the interstitial water in porous sediments to parts of the oceanic or lacustrine water column and all the way up to the redox-state of the world's ocean-atmosphere system.

In contrast to anoxia, oxic conditions reflect the presence of free oxygen. Quantification of O_2-abundance for the geological past frequently refers to a percentage of the present day atmospheric level of oxygen (PAL O_2).

Somewhat more loosely defined in terms of its O_2-abundance are redox-states such as suboxic or dysoxic. However, common sense tells us that these attributes characterize an environmental situation between oxic and anoxic conditions.

Finally, the term "anoxia" is frequently utilized interchangeably with the term "euxinic". Euxinic conditions, however, refer to a water column, which contains dissolved hydrogen sulphide.

L. N. Neretin (ed.), Past and Present Water Column Anoxia, 3–19.

Following Berner's original classification of sediments [8], oxic sediments are deposited under an O_2-concentration greater than 30 μM, suboxic sediments are characterized by O_2-concentrations between 30 and 1 μM O_2. Anoxic sediments with less than 1 μM O_2 were differentiated into non-sulphidic ($H_2S < 1\ \mu$M) and sulphidic ($H_2S > 1\ \mu$M) deposits.

Any earth science text book contains ample descriptions of anoxia, even global anoxia. For example, we view the distant past, the early part of earth's history (the Archaean) as a world, in which the entire ocean-atmosphere system was anoxic, followed by a Great Oxygenation Event and subsequent oxygenation of atmospheric, surface and deep water environments [29, 30]. However, alternative views are also considered [51]. Prolonged deep ocean anoxia has also been proposed for the early Paleozoic [12]. Multiple levels of black shale deposition during the Cretaceous are described as oceanic anoxic events (OAEs) with global implications [3]. Large scale, possibly global anoxic conditions have been considered as cause for mass extinctions [88]. Finally, numerous modern oceanic settings show anoxic/euxinic water column conditions [21].

On a smaller scale, any sedimentary environment contains a transition from oxic to anoxic conditions as reflected by decreasing oxygen abundance with depth. Pertinent lithological (e.g., grain size) and biological (e.g., bioturbation, microbial activity) characteristics determine how steep this gradient is and how quickly the pore waters become anoxic.

Considering these examples, it is obvious that any discussion of anoxia, in particular with respect to the geobiological consequences, will strongly depend on the scale of observation. This contribution will focus on large scale anoxia, affecting the entire or at least large parts of the atmosphere-ocean-system. Following a previous comprehensive account of modern and ancient anoxia [5], it is the aim of this review to update and extend the temporal record of global anoxia.

2. MODERN ANOXIA

A long history of continuous research in modern anoxic environments has significantly improved our understanding of causes and consequences of water column anoxia. Based on differences in the oceanographic framework, three different types of marine anoxic environments have been suggested [21]: (a) silled basins, (b) upwelling zones and (c) stable oxygen minimum zones in the open ocean. Prominent examples include (a) the Black Sea, the Baltic Sea, the Cariaco Basin, the Framvaren Fjord, or the Saanich Inlet; (b) the South-West African shelf off Namibia, or the Peruvian/Chilean shelf, and (c) the Arabian Sea and northern Indian Ocean, or the Gulf of California, respectively. Results for some of these settings will be presented in this volume, and will not be repeated here.

The central observation made in all studies of modern anoxic environments, however, should be emphasized here as well. Modern anoxic environments reflect the interplay between the two principal causes for anoxia: the delivery of large quantities of fresh organic matter to the deeper part of the water column, causing a high oxygen demand (aerobic respiration), and an oceanic circulation that is incapable of supplying sufficient quantities of dissolved oxygen to satisfy this demand.

Tracing anoxia through time can only be achieved on the basis of geological, biological and geochemical proxies that allow to differentiate anoxic from oxic conditions. These will be introduced in the following paragraph.

3. PROXIES FOR ANOXIA

Evidence for anoxic vs. oxic conditions, both in the atmosphere as well as the hydrosphere, includes geological and paleontological indicators that are entrained in the sedimentary rock record and readily available during field inspection. Equally important, however, are abundances or ratios of redox-sensitive elements such as C, S, Fe, Mo, U, Th, and others. Furthermore, the stable isotopic composition for some of these elements (C, S, N, Fe, Mo) provide evidence for (bio)geochemical cycling under changing redox conditions. Finally, organic geochemical evidence, specific biomarkers indicate biologically mediated processes in the water column and or the sediment.

It is beyond the scope of this contribution to fully evaluate the validity of every indicator listed above. Instead, all will be briefly introduced with the pertinent literature provided for further reference.

3.1 Geological and Paleontological Indicators

Already in the 1960s, a qualitative assessment of earth's oxygenation through Precambrian time was achieved [20], considering a variety of – now classical – sedimentary rocks and minerals (for review see [30]). All were deposited in surface or near-surface environments and would, thus, attest to the presence or absence of oxygen in the atmosphere-hydrosphere-system. Such proxies include detrital uraninite (UO_2) and detrital pyrite (FeS_2) in late Archaean sediments from the Witwatersrand Supergroup, South Africa (less-oxidizing atmosphere), Superior-type banded iron formations of late Archaean and Paleoproterozoic age in southern Africa, western Australia and North America (deep water anoxia overlain by oxic surface water), oxidized paleosols and red beds in Paleoproterozoic successions of southern Africa and North America (oxidized atmosphere), Meso- and Neoproterozoic sulphate occurrences oxidized atmosphere and surface water) and Metazoan life during the terminal Neoproterozoic (oxidized atmosphere and surface water).

In more general terms and applicable throughout earth's history, the deposition of black shales, organic carbon and pyrite-rich siliciclastic sediments, is attributed to anoxic conditions in (larger) parts of the water column [89]. Such conditions of bottom water anoxia are further supported through the absence of bioturbation as indicated by the lack of trace fossils.

In addition, the size distribution of sedimentary pyrite is increasingly being utilized as a proxy signal for water column anoxia [91]. Microframboids formed in a necessarily anoxic water column are distinctly different in size and shape compared to diagenetic (even more so late diagenetic) pyrite formed in the sediment.

3.2 Geochemical Proxy Signals: C-S-Fe

The biogeochemical cycling of redox-sensitive elements in sedimentary environments results in characteristic changes in their abundances and ratios. One of the key processes in marine sediments is the anaerobic mineralization of sedimentary organic matter through fermenting and subsequently sulphate reducing bacteria. Sulphate is reduced at the expense of organic matter which is oxidized, thereby buffering the atmospheric oxygen abundance [9]. This is expressed in a positive correlation between the abundances of organic carbon and pyrite sulphur, a traditional proxy signal for normal marine, i.e. oxic bottom water [11, 43, 61, 62] vs. semi-euxinic and euxinic bottom water conditions [61]. Subsequently, it was realized that the availability of reactive iron was an additional important parameter in euxinic environments [63, 64]. No positive correlation between organic carbon and pyrite sulphur can be observed in such sediments.

Apart from C-S-Fe systematics described above, substantial effort has been devoted to a detailed quantification of different sedimentary iron species [60, 64]. Depending upon analytical data, two parameters were defined:

the degree of pyritization (DOP)

$$DOP = Fe_{PYR}/Fe_{PYR} + Fe_{HCl}$$

the degree of anoxicity (DOA)

$$DOA = (Fe_{PYR} + Fe_{MAG} + Fe_{OX} + Fe_{CARB})/Fe_{T}.$$

Both allow anoxic depositional conditions to be distinguished from oxic conditions. A DOP value less than 0.45 reflects deposition under normal marine, well-oxygenated bottom water conditions, whereas a DOP > 0.75 suggests anoxic bottom water conditions. Intermediate values are thought to reflect dysaerobic or dysoxic conditions with low O_2, but no H_2S [63]. Alternatively, a DOA > 0.38 has been shown to reflect deposition beneath anoxic bottom water conditions [59].

3.3 Trace Element Abundances and Ratios

Abundances and ratios of redox-sensitive trace elements are frequently utilized to assess the redox conditions of modern and ancient sedimentary systems [37, 49, 76]. Classical examples include V, Cr, Ni, Co, Mo or U, all reacting differently under varying oxygen content, thus representing valuable proxy signals particularly in laminated sediments. A positive correlation with organic carbon abundances is further consistent with the aspect of enhanced preservation of organic matter and enrichment of numerous trace elements under anoxic conditions (for a recent review see [37]).

In addition to trace element abundances, the isotopic composition of selected redox-sensitive elements like molybdenum represents an equally powerful indicator for anoxia [1].

3.4 Biomarker Evidence

Biomarkers are molecular fossils which can be found in sediments/sedimentary organic matter and which reflect the former presence and metabolic activity of living organisms [24, 58]. Organic geochemical methods provide the means for identifying the precursor organisms but also for characterizing the depositional environment and/or bacterial and inorganic degradation during diagenesis. For the present discussion, the prevalence and extent of anoxic conditions in the water column of a sedimentary environment is the prime question. Undoubtedly, the anaerobic microbial reworking of sedimentary organic matter, either in the sediment or in anoxic bottom waters, is an important process in sedimentary environments. However, the ability to reconstruct photic-zone anoxia would indicate a possible contribution of anaerobic organisms to primary productivity via anoxygenic photosynthesis.

Unequivocal evidence for anoxic water conditions within the photic zone is provided by the presence of bacterial pigments (such as isorenieratene) which are uniquely biosynthesized by strictly anaerobic bacteria. The presence of isorenieratene and derivatives, together with their characteristic carbon isotopic composition, point to the (former) activities of photosynthetic green sulphur bacteria (Chlorobiaceae) which live under low light intensities and sulphide dissolved in the water column. Clear indications for anoxygenic photosynthesis exist in recent environments, such as the Black Sea (e.g. [67]), but evidence is growing also from ancient sedimentary environments, like the Mediterranean sapropels of Pliocene age (e.g. [14, 53]), Cretaceous sediments from the North

Atlantic (e.g. [81]), Jurassic black shales in Europe (e.g. [75, 77, 83]) or Devonian and Silurian rocks from Europe and North America (e.g. [36, 85]).

Additional biomarker evidence for paleoredox conditions during sedimentation includes the lycopane/C_{31} *n*-alkane ratio (e.g. [82]). Assumed to be derived from a photoautotrophic organism, high abundances of lycopane (with a characteristic carbon isotope signature) in modern and ancient sediments deposited from anoxic water column conditions attest to its preferential preservation under oxygen-deficient conditions. This selective preservation results in an increase of the lycopane/C_{31} *n*-alkane ratio, which provides a respective proxy signal for palaeoxicity.

4. ANOXIA IN THE GEOLOGICAL PAST

4.1 The Precambrian World

Qualitatively, the notion of an anoxic world during the early part of Earth's history (Fig. 1) is based in part on our understanding that the early atmosphere was largely reducing, containing CO, NH_3, H_2, all inorganic compounds from which the early building blocks of life could have been generated [47]. With regard to quantitative aspects, two strongly opposing models have been proposed in the past: a three stage model with the consecutive oxygenation of the atmosphere, surface water and deep water [29, 39] and an invariable abundance of atmospheric oxygen for the past 4 Ga, possibly within 10 % of the present days atmospheric level [51].

This longstanding controversial discussion whether or not the Archean and early Paleoproterozoic ocean-atmosphere-system contained substantial amounts of free oxygen has recently moved forward by a new "piece of evidence", notably the discovery of mass-independent sulphur isotope fractionation, recorded in sedimentary sulphide and sulphate. Independent of the precise mechanisms it appears that the photochemical dissolution of sulphur dioxide is the principal cause for mass-independent sulphur isotope fractionation. The fact that such signals have been measured in near-surface sedimentary sulphide and sulphate indicates an "oxygen free" atmosphere. Otherwise, oxidation of reduced atmospheric sulphur species, rainout of these as sulphate and subsequent homogenization of this signal in the ocean would have resulted in the loss of such a signature. However, a very distinct record of mass-independent sulphur isotopes exists [7, 26, 48, 52], thereby pointing to an atmospheric oxygen abundance of $<10^{-5}$ PAL [57]. Evidence for significant mass-independent sulphur isotope fractionation is absent in sedimentary rocks younger than 2.32 Ga, based on a sulphur isotope study of sedimentary pyrite from the Transvaal Supergroup, South Africa [7]. This in turn suggests, that the atmospheric oxygen abundance increased at 2.32 Ga, possibly from $<10^{-5}$ to 10^{-2} PAL O_2.

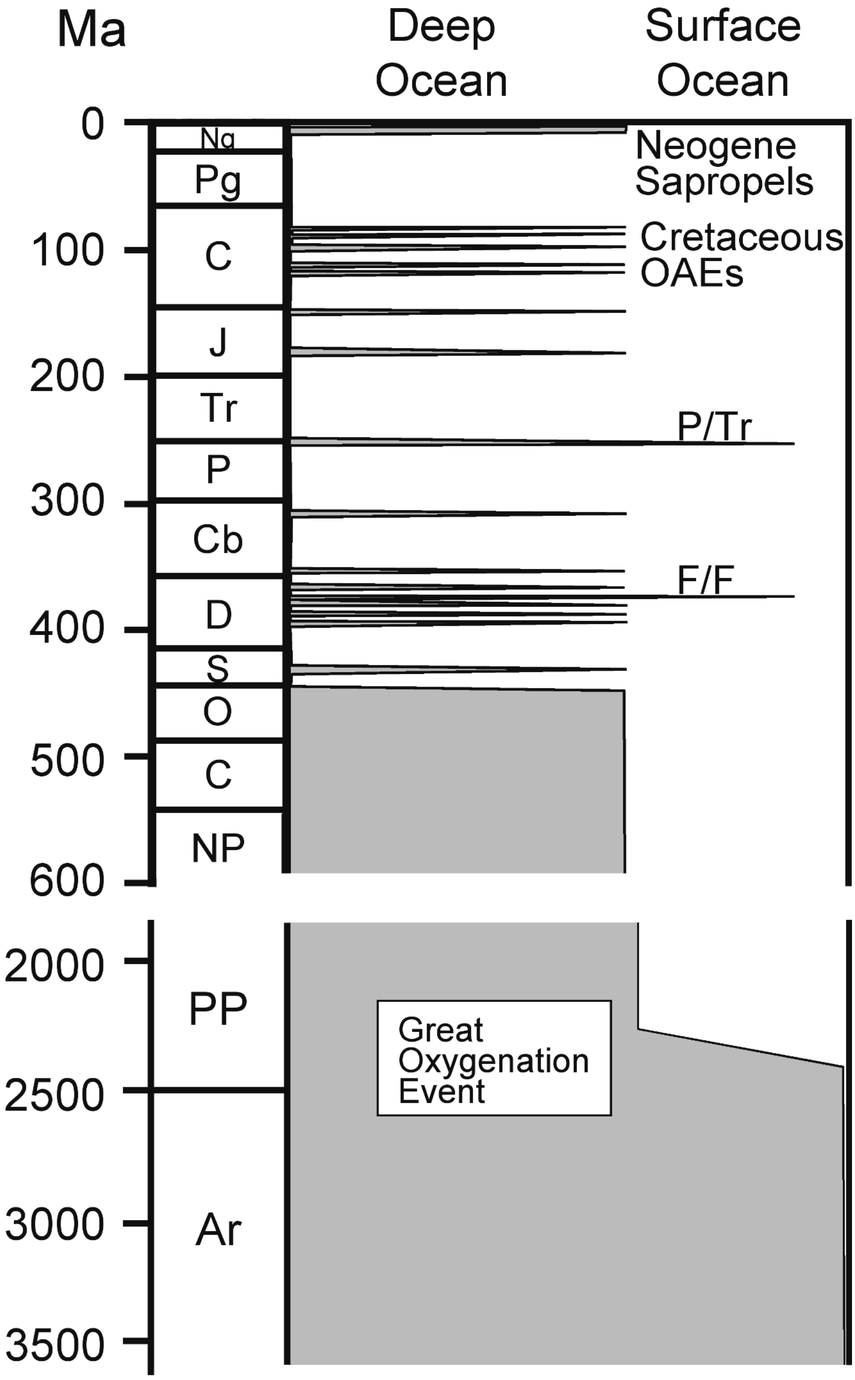

Figure 1. Temporal record of widespread anoxic conditions (grey shaded area) in the shallow and deep ocean (see text for source of data).

Evidence for a stepwise increase in the atmospheric oxygen abundance can be further obtained from long-term isotope records. Secular variations in the isotopic compositions of carbon, oxygen, strontium and sulphur in seawater are believed to faithfully reflect the evolution of the ocean-atmosphere system. While the strontium isotopic composition records temporal variations in the proportional inputs from continental weathering and high-temperature basalt-seawater reactions at mid-ocean ridges, carbon and sulphur isotopes react to biologically mediated redox reactions, resulting in changes of the fractional burial of reduced (organic C, pyrite S) vs. oxidized (carbonate C, sulphate S) compounds. Finally, oxygen isotopes are a proxy signal for climatic changes.

Respective isotope records have been determined with high temporal resolution for the Phanerozoic [38, 87] and with substantially less detail also for the Precambrian [45, 80, 84]. The seawater strontium isotopic evolution clearly displays two periods with a steep increase, between 3.0 and 2.0 Ga and between 0.8 and 0.55 Ga, respectively. Major tectonic rearrangements, resulting in an increasing contribution of radiogenic strontium, are the likely cause for this pattern [28]. The first time interval represents a period in Earth history of significant growth of continental crust whereas the Neoproterozoic shift in ^{87}Sr/^{86}Sr reflects the break-up of Rodinia. Both processes would result in a net increase of near-shore shelf habitats. Interestingly, the same time intervals also display an overall ^{13}C enriched carbonate carbon isotope signature [32, 46], sharply punctuated by shifts to negative $\delta^{13}C_{carbonate}$ values during intervals of glaciation. Mass-balance considerations suggest that these ^{13}C enriched values reflect an increase in the fractional burial of organic carbon [32] and/or alternatively a prolonged residence time of organic matter in the water column [70]. An increase in the fractional burial of organic carbon, however, translates into an increasing contribution of oxygen to the atmosphere, resulting in the proposed stepwise oxygenation of Earth's atmosphere [22]. Less well constrained, but still discernible, are shifts in the sulphur isotope record. In particular the terminal Neoproterozoic and early Cambrian display a strongly positive δ^{34}S signature of seawater sulphate [84]. Again, mass balance considerations suggest a higher fractional burial of reduced (biogenic) sulphur, and consequently less oxygen demand.

Recently, a new model for Proterozoic ocean chemistry [18], notably the drawdown of dissolved Fe from Proterozoic oceans as iron sulphide, has been proposed. Sulphide sulphur isotope data from Mesoproterozoic successions have been provided as evidence for a proposed anoxic if not sulphidic Paleo- and Mesoproterozoic deep ocean [60, 79]. It was suggested that oxygenation of deep ocean waters occurred not earlier than the early Neoproterozoic, consistent with earlier views on the emergence of sulfur disproportionation [19].

4.2 The Early Paleozoic

Following the break-up of Rodinia, the early Paleozoic world was characterized by a large continental area (Gondwana) above the South Pole and dispersed continents (such as Laurentia, Baltica, Siberia and others) in low and mid-latitudes [78]. An overall high sea level resulted in the flooding of large continental areas and the development of distinct facies variations including the deposition of extensive laminated non-bioturbated sediments (black shale deposits). Abundant occurrences, such as Cambrian varved black shales [94], the Ordovician and Silurian graptolite shales [12] or Devonian and Carboniferous black shales deposits [25] on many continents suggest deposition from an apparently oxygen deficient deeper part of the water column during much of early and middle Paleozoic times (Fig. 1). Combined sedimentological and paleontological evidence was utilized to propose a model for different facies developments and animal habitats in the early Paleozoic [13]. This shows the spatial distribution of proximal oxic, bioturbated sediments, termed shelly facies, followed by distal non-bioturbated, anoxic, pyritic black shales of the so called graptolite facies. Analogous to modern anoxic settings, the water column would have contained a chemocline and a distinct vertical sequence of primary productivity in the photic zone, followed downward by aerobic respiration, denitrification and sulphate reduction. The lateral extent of this facies distribution was dependent on the prevailing climatic conditions which were responsible for changes in sea level but more importantly for an initially sluggish oceanic circulation. Progressive ventilation of the early and mid-Paleozoic oceans with oxygen is viewed as a consequence of growing ice sheets in the high latitudes and a subsequent ocean circulation comparable to the modern world.

Additional evidence stems from temporal variations in the carbonate carbon [87] and sulphate sulphur [38] isotopic composition. Isotope mass balance calculations based on these records suggest enhanced anaerobic respiration of sedimentary organic matter via bacterial sulphate reduction, consistent with a view of oxygen-deficient bottom waters.

Apart from an overall appearance of (possibly) prolonged oxygen deficiency in the early and mid-Paleozoic deep ocean, evidence has been provided for a link between anoxia and extinction events during this time interval [35, 40, 90].

4.3 The Permian-Triassic Transition

Numerous causes have been proposed for the greatest mass extinction during Earth history at the Permian Triassic boundary (e.g. [6, 41, 42, 66, 71, 93]). Among them, widespread end-Permian oceanic anoxia (Fig. 1) is indicated by respective laminated organic and pyrite rich black shales from shallow and deep water environments [92].

Modeling results (general circulation model combined with oceanic biogeochemistry, specifically nutrient transport) suggest sluggish ocean circulation and the development of widespread anoxia in the deep ocean as a consequence of a low equator to pole temperature gradient and the enhanced export of phosphate to the deeper ocean [31]. However, nutrient limitation causing a reduced primary productivity prevents prolonged sulphidic deep water conditions.

In contrast, numerous sedimentary basins comprising pyritic black shale successions exhibit petrographic, geochemical and sulphur isotopic data in favor of sulphidic deep water during the late Permian and its transition into the Triassic (e.g. [50]). In fact, a significant drop in the atmospheric O_2 abundance has been attributed as a cause for a collapse of the marine ecosystem at this time boundary with an emphasis on reef communities [89].

Finally, perturbations of the global carbon cycle suggest a combination of a shift in magnitude and locality of organic carbon burial, from high burial of terrestrial and marine organic matter during late Paleozoic time to low and primarily marine organic carbon burial in the Triassic and thereafter [10]. A reduced level in atmospheric oxygen would be the predicted consequence. Superimposed on this is a proposed sudden release of methane [71], as indicated by a short-term, high-magnitude shift towards negative δ^{13}C values (e.g. [42]).

4.4 Jurassic and Cretaceous Black Shales (OAEs)

The widespread deposition of organic-rich black shales characterizes early Jurassic and Mid-Cretaceous times (Fig. 1), with numerous examples from present-day continental areas and in DSDP/ODP cores. The observation of an apparently time-equivalent deposition of this distinctive lithology during relatively short-term intervals on several continents suggested a global phenomenon and, hence, a common cause. Initially coined for the Mid-Cretaceous, these globally correlative short-term (less than 1 million years) levels of black shale deposition were termed “Oceanic Anoxic Event (OAE)” [73]. Extensive research over the past decades produced a wealth of information which centered on the following issues (e.g. [27, 33])::

Paleoceanography, Sea level changes, Paleoclimate

Organic and inorganic geochemistry

Implications for global geochemical cycles

A generally warm climate, relatively high sea level, a proposed high abundance of atmospheric carbon dioxide and climate induced oscillations in precipitation and continental run-off causing salinity stratification resulted in extended epicontinental seas characterized by sluggish deep water circulation and persistent deep water anoxia. One of the consequences was the enhanced deposition and preservation of organic matter, the latter visible on a global scale by shifts to positive carbonate δ^{13}C values (e.g. [4, 34, 74]). Well preserved organic matter allows the detailed reconstruction of primary productivity and secondary mineralization of sedimentary organic matter. For the lower Jurassic Toarcian black shales of Europe for example, organic geochemical data (biomarker, compound-specific organic carbon isotope data) indicate oscillations in the depth of the chemocline suggesting recurring periods of anoxygenic photosynthesis (e.g. [75, 77]).

4.5 Neogene Mediterranean Sapropels

The Mediterranean Neogene sedimentary record contains abundant examples of centimeter to decimeter thick dark laminated layers containing up to 30% organic carbon (for review see e.g. [68]). These so called sapropels were deposited most prominently during Pliocene and Pleistocene time, predominantly but not exclusively in the eastern Mediterranean (Fig. 1). Sapropel formation is thought to be a consequence of sluggish deep water ventilation as a result of a stable pycnocline which affected much of the late Miocene to early Holocene Mediterranean Sea. The latter was induced by climate-driven enhanced river flow from Eurasia and Africa into the Mediterranean causing a strong salinity difference. Strongly contrasting views exist with respect to surface water nutrient availability and resulting levels of primary productivity (e.g. [16, 72]). Subsequent degradation of sinking organic matter, in addition to the salinity gradient, forced the establishment of a stagnant deep ocean. It has been proposed that climate-driven sapropel formation is ultimately linked to variations in the precession, which occur about every 21000 years (e.g. [69]).

Apart from the distinct lithology, ample biogeochemical and isotopic evidence exists for the sapropel formation (e.g. [15, 54–56]), but also extending into the photic zone [53].

5. SUMMARY

Multiple times in Earth history, anoxic conditions were prevailing in large parts of the ocean. The occurrence of widespread, possibly global oceanic anoxic conditions is a consequence of different factors interrelated with each other including the evolving oxygenation of Earth's surface environments, climate-induced differences in oceanic circulation and increased primary productivity causing an enhanced oxygen demand in the water column. The temporal record of water column anoxia is resolvable to different levels of detail, ranging from globally representative long-term seawater isotope records of carbon, sulphur, and to a lesser degree of nitrogen, to organism-specific molecular information and compound-specific organic carbon isotope work.

The temporal record of anoxia suggests a largely anoxic Precambrian world in which the oxygenation of the atmosphere and the surface ocean occurred