

The oxygen state of the oceans of Proterozoic eon

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The rise of oxygen in early earth's atmosphere and oceans is a much-discussed subject, and today opinion is much divided on many of its aspects, particularly about when this occurred. Based on a variety of available geological records, which have significant bearing on the status of oxygen and carbon dioxide, like the occurrence of banded iron formations (BIFs), deposits of uraninite (UO_2), pyrite (FeS_2) and siderite (FeCO_3), palaeosols (ancient soils derived from rock weathering), besides evidences from studies on isotopes of C, S, Mo and O (mass-dependent and mass-independent fractionations), two opposing views are much discussed today¹⁻⁸. One of them claims that prior to 2.3 billion years (b.y.) ago, oxygen was low or absent in the atmosphere and rose rapidly between 2.25 and 2.05 b.y. ago, while the second model postulates that the atmospheric oxygen level was essentially constant since 3.5 b.y. ago^{3,4}. However, opinion does not seem to be much divided that the oxygenation of the oceans, through atmosphere-ocean oxygen exchange, was less vigorous and fluctuating till much later geological times^{1,9}.

According to a model proposed by Canfield¹⁰, the transition of the oxygen chemistry of the oceans, from an anoxic Archaean eon (3.8–2.5 b.y.) to an oxic one at about 0.54 b.y. ago (Palaeozoic) was not abrupt, but went through a state of intermediate oxygenation during the long intervening Proterozoic eon (2.5–0.54 b.y.). Commencing sometime after 1.8 b.y. ago, surface waters of the oceans were oxic and bottom waters were anoxic (sulphidic or euxenic), a state that is believed to have lasted for about a billion years. Canfield developed his model based on the geochemical behaviour of redox-sensitive elements like U, Fe and S in the oceans of Archaean and subsequent periods, notably from the occurrence of large pyrite (FeS_2) deposits. According to him, these deposits were products of anaerobic bacterial reduction of the sulphates dissolved in the ocean waters to sulphides, the latter subsequently reacting with iron to form FeS_2 . The reactions to form pyrite were helped by liberal additions of iron (Fe^{2+}) from sea-floor hydrothermal

vents and abundant sulphates and metabolizing organisms as well as some iron from intense terrestrial weathering of ancient cratons which were in the process of merger to form the early supercontinents^{4,5,9,11-13}. These sulphate-reducing bacteria thrive only under anoxic environment, and hence pyrite deposition is expected to be high in anoxic or euxenic waters and low in oxic waters, a feature that has been used by several investigators to model the oxygen state of ocean waters.

Recently, Shen *et al.*¹⁴ used the above environment-sensitive biochemical reduction to form FeS_2 , expressed as degree of pyritization (DOP)⁵, as a guide to know the redox state of the mid-Proterozoic oceans and also employed the sulphur isotope ratios in the pyrites to interpret their sulphate chemistry. Their studies were carried out on pyrites from the 1.5 to 1.42 b.y. old black shales formed west of the Gulf of Carpentaria (Australian Northern Territory), an intracratonic basin in contact with the global ocean of the period. Here, the DOP in sediments formed at different ocean depth zones (inner shelf shales, distal shelf facies and basinal environment) was observed by them to be distinctly different – low in the shallow near-shore sediments and high towards offshore or deep-ocean basin sediments. Such a trend, they explained, was due to prevalence of euxenic conditions at the bottom of the oceans and oxic conditions near the surface, which, they said, demonstrated the existence of two distinct water masses, when these sediments were laid down in the ocean bottom.

In recent years, fractionation trends exhibited by the stable isotopes of S, C, Mo and O present in minerals known to have been precipitated from the ocean waters of Archaean and Proterozoic eons are increasingly being employed to trace the redox state of oceans of this age and to find the specific modes of their release from host rocks before they reached the ocean^{6,7,15,16}. Basically, during the biochemical reduction process to form pyrite, the normal ratio between the two isotopes of sulphur – S^{32} and S^{34} – is offset by the preference of the anaerobic bacteria to the lighter of the two isotopes

and this leads to strongly 'depleted' sedimentary pyrite relative to co-existing sulphate of the same age in sea water. Further, from culture experiments it is found that their isotopic fractionation is controlled by the concentration of sulphates in the waters and speciation of iron^{6,17}. Now Shen *et al.*¹⁴ have used the characteristic geochemistry of S-isotopes in the pyrites to further interpret the chemistry of mid-Proterozoic oceans.

In their investigation of the Australian samples, Shen and his team found a regular variation of S-isotopes in the pyrites (expressed as $\delta^{34}\text{S}$) along the palaeo-environmental gradient, from proximal shore region to distant offshore samples, the most negative $\delta^{34}\text{S}$ values occurring in the basinal shales and the most positive $\delta^{34}\text{S}$ along the coastal environments. They have related this to low sulphate concentration gradient that must have existed between coastal and offshore regions till the close of Proterozoic eon and have further deduced that probably oxygen in the atmosphere also may have remained well below present levels¹⁶, resulting in ocean bottom anoxia. They have also reported additional evidences for such a state of ocean bottom anoxia from two more regions belonging to older 1.73–1.64 b.y. period elsewhere in Northern Australia, showing strongly enriched $\delta^{34}\text{S}$ data in pyrites. These findings are taken to imply the existence of low sulphate and basinal euxenic ocean conditions¹⁴ in Proterozoic earth for more than 250 million years (between 1.73 and 1.44 b.y. ago). Similar high $\delta^{34}\text{S}$ and low sulphate waters are also observed in coeval (~1.47–1.44 b.y.) shale in North America, and in much younger carbonates¹⁶ from Namibia. Based on these observations, they conclude that positive $\delta^{34}\text{S}$ values characterize early diagenetic pyrites from mid-Proterozoic shelf shales around the world and that marine sulphate levels may have remained low until the end of the Proterozoic eon.

In another approach to the same problem about the redox state of the Proterozoic oceans, Arnold *et al.*¹⁸ relied upon Mo stable isotopes since they felt that DOP and S-isotope fractionation data used by earlier workers are not as robust

indicators of ocean anoxia as the isotopes^{19,20} of Mo. Further, they feel low sulphate ocean conditions and redox-stratified sedimentary basins are not unique for the Proterozoic, as such a state is known to exist even today where oceans are well oxygenated top to bottom. Molybdenum, as MoO_4^{2-} anions, is transported to the oceans by rivers and removed from the sea water under anoxic or sulphidic conditions into pyrites and under oxic conditions into ferromanganese oxide sediments by diffusion across sediment–water interface and immobilized there^{21–23}. Molybdenum fractionation ratio (expressed as $\delta^{97/95}\text{Mo}$) is the same in sea water and in the sulphide sediments suggesting that Mo isotope composition of sea water depends on the extent of adsorption into the oxic sediments. Since the $\delta^{97/95}\text{Mo}$ in sea water can vary consistently with changes in relative proportions of anoxic and oxic sedimentation in oceans, the Mo system can be a good tool to interpret the palaeoredox state of the oceans²³. Therefore, if the area of oxic sea water were smaller in the past, $\delta^{97/95}\text{Mo}$ in the marine black shale is expected to shift toward lighter values.

Arnold *et al.*¹⁸ examined the mid-Proterozoic marine shale samples from the same areas studied by earlier workers¹⁴ and found that the $\delta^{97/95}\text{Mo}$ in sea water was significantly lighter than in modern equivalent euxenic sea-bottom (e.g. Black Sea sediments), suggesting that the Mo-isotope budget during mid-Proterozoic was quite different from modern times and that that redox conditions in mid-Proterozoic ocean floor differed from that of the present day. Based on their Mo-isotope data, they have concluded that the area of euxenic sedimentation in the mid-Proterozoic was 10 times larger than in present day and they believe that such euxenic conditions of deep ocean may have persisted for a long period until after 1.0 b.y., when there was improved atmosphere–ocean oxygen exchange^{6,10} and ocean anoxia may have been restricted thereafter to a few places¹⁹.

These interesting findings in marine black-shale sediments undoubtedly reveal the potential of bio-geochemical reactions combined with isotope fractiona-

tion data to improve our understanding of palaeoenvironment and its biology^{6,9}. Whether the inferences from such applications are valid merely for the local ocean condition or could be true globally, can be established only through data from several other Proterozoic marine sediments around the world. Interestingly, apart from these data from Australia and North America, both of which were lying separated in the Proterozoic supercontinent assembly Rodinia¹³, a report about existence of ocean anoxia inferred from $\delta^{34}\text{S}$ data in Proterozoic age uraniferous black shales and phyllites from Rajasthan in India²⁴, which, during this period was located far away from either Australia or North America, may suggest that the ocean bottom anoxia may have been widespread, possibly global in its coverage. Next, the question still remains whether the enriched values and decreased sulphur fractionations could be due to low sulphate in water or lack of sulphate-reducing bacteria or due to other factors that affect its concentrations in oceans, such as sulphate generation routes or sea-level fluctuations arising from intermittent spells of glaciation during Proterozoic²⁵, affecting areas of coastal shelves^{15,26}. Likewise, Mo isotope record may be influenced by changes in Mo input by rivers or by poor scavenging under mild euxenic conditions or due to lack of connectivity between euxenic basins and global oceans¹⁹. Nonetheless, the spate of recent studies have unequivocally supported prolonged existence of intermediate state of ocean-oxygen that followed in the wake of influx of oxygen in the atmosphere early in Proterozoic. This should help achieve better understanding of the rise of oxygen in the earth's atmosphere, an issue that has kept the proponents of the two major opposing models on this problem firm in their respective views.

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