

Early Proterozoic (2.5–2.3 Ga) oxygen revolution on the earth superseded? New findings indicate oxygen build-up 700 million years earlier

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The rise of oxygen in the earth's atmosphere and oceans continues to be one of the much-discussed, unsolved subjects in earth science despite considerable data emerging from several lines of research on this issue. Investigations on a variety of geologic materials like the banded iron formations (BIFs), deposits of uraninite, pyrite and paleosols, besides studies on the isotopes of S, C, O and Mo have led to the view that prior to 2.3 billion years (b.y.) ago oxygen was low or absent. Thereafter it is believed to have risen rapidly between 2.25 and 2.05 b.y. ago, a period considered to signify the 'Great Oxidation Event' (GOE) or 'Oxygen Revolution' on the earth which is also supposed to have heralded the beginnings of the photoautotrophs or organisms like the cyanobacteria, the main producers for the earth's oxygen¹⁻⁴. These photoautotrophs derive their energy by photosynthesis in the photic zone of the sea using water as electron donor and produce oxygen as a waste product of their cellular functions. The main issue, which has generated considerable research and debate in recent years, is about the generally accepted timing of the evolution of oxygenic photosynthesizing bacteria on the earth. Though several fossil discoveries of cyanobacteria and allied organisms belonging to the early Archaeans were reported, most of them were discredited as their biogenicity and antiquity came to be disputed⁵. Thus, the consensus that the GOE marked the arrival of the oxygen producing organisms on the earth prevailed.

According to the established thinking, the earth's atmosphere and the oceans were anoxic during early Archaean to early Proterozoic (3.85–2.45 b.y. ago) till the 2.45–1.85 b.y. span, when oxygen production commenced. However, most of it was absorbed in the oceans and consumed in oxidizing the dissolved Fe, Mn, U to form their well-known seafloor deposits. While these metals gradually depleted in the oceans due to conversion to their insoluble oxides, oxygen production continued uninterrupted resulting in

its accumulation in the atmosphere by around 1.85 b.y. ago. Oxygen, being a poison for the cyanobacteria, the upshot of this trend led to their extinction and forced a lull in oxygen production. By late Neoproterozoic, about 540 million years ago, a balance between build-up of oxygen and its exchange with the oceans could be achieved enabling cyanobacteria to flourish once again¹.

The dominant perception about the rise of oxygen in the atmosphere only after 2.3 b.y. ago as well as linking the arrival of oxygenic photosynthesis with the GOE, however, is doubted by a section of geoscientists. They believed that photosynthesizing bacteria had flourished much earlier and that the atmosphere was oxygenated up to $\pm 50\%$ its present atmospheric level (PAL) even during the early Archaean (3.6–3.2 b.y.)⁶⁻⁹. This latter view did not gain much popularity, but a recent find of sedimentary hematite crystals, formed evidently by the oxidation of dissolved Fe^{2+} in the deep domains of an oxygenated sea around 3.46 b.y. ago, has now rejuvenated this group's model besides contradicting the entrenched view that the seas were anoxic during this period¹⁰. This mineralogical pointer to Archaean oxygenation is from banded iron-bearing cherts belonging to early Archaean Marble Bar Cherts (MBC) in the Pilbara Craton in Western Australia. Unlike the questionable biological evidences advanced during earlier years, this new find formed the basis for the conclusion that atmosphere-ocean oxygen exchange was active and that oxygenic organisms had evolved some 700 million years prior to the widely accepted 2.5 b.y. date for their arrival.

Archaean oceans were rich in dissolved iron (Fe^{2+}) mostly derived from weathering and erosion of early continental rocks. Besides, there was also large additions of iron from submarine hydrothermal vents, midocean ridges and seamounts. Chemically, the dissolved Fe^{2+} in water is unstable in the presence of O_2 in the seawater with which it combines to form Fe^{3+} -ferric oxide and Fe^{3+} -

hydroxide and precipitates as seafloor deposits. Dissolved iron as Fe^{2+} and $\text{Fe}(\text{OH})^+$ exhibit another mode of oxidation at relatively shallow depths within the anoxic photic zone of the sea, where they absorb ultraviolet (UV) radiation and form ferric iron and Fe-hydroxide $\text{Fe}(\text{OH})_2$. This reaction is aided by the absence of ozone layer, which can screen the intense UV radiation so pervasive during early earth times. This photooxidation of Fe^{2+} is also promoted by the thriving anaerobic iron-oxidizing bacteria (photoferrotrophs) which derive their energy from iron and very poor light prevailing at moderate depths of the sea^{11,12}.

The hematite-rich Australian Marble Bar Cherts (50–200 m thick) occur as parallel microbands extending lengthwise for about 30 km and lie between two layers of basaltic rocks, products of submarine volcanism, the older of which erupted around ~ 3.474 – 3.463 b.y. ago and the younger one ~ 3.46 – 3.455 b.y. ago. The materials for the sedimentary formations were deposited in a large ($\sim 30 \times 50$ km) basin, estimated to be >200 m, possibly up to 1000 m deep, and created perhaps as a result of volcanic collapse during the closing stages of the older volcanic episode. The sediments must have been deposited during periods of quiescent volcanism as evidenced by (i) the absence of any textural signs of weathering and erosion or disruption by waves and currents on the entire erosional surface (ii) absence of features denoting explosive subaqueous volcanism in the form of tuff breccias, pillows or vesiculated-pillows in the volcanic sequence, suggesting their formation under the high pressure of the overlying mass of sea water. Subsequent to the younger volcanic episode, the sediments forming MBC underwent deformation between 3.4 and 2.9 b.y. ago and was tilted vertically making the units of this formation younger with depth.

Detailed electron microscopic and electron diffraction studies¹⁰ of the hematite have revealed that they are not aggregates of sub-microscopic particles

of ferric hydroxides but are 0.1 to ~1 μm sized single crystals that had nucleated at a depth of >200 m at a temperature above 60°C directly from submarine Fe^{2+} -rich hydrothermal plumes in the well-oxygenated water. In many of the ancient rocks, hematite is also known to form by the oxidation of siderite (FeCO_3) by O_2 -rich groundwaters at the surface or by photooxidation in near-surface environments and thereafter sink to the bottom. However, the siderite bearing chert examined are samples from drill-cores obtained from depths far below the water table and the photic zone. Also, mineral paragenetic studies and other findings under electron microscope indicate that the hematite had crystallized much before the siderites that occur alongside. The siderites here have apparently formed when Fe^{2+} rich hydrothermal solution reacted with abundant CO_2 present in the seawater and do not appear to be products of photooxidation.

The composite picture presented by various studies on the hematite crystals from the 3.4 b.y. old Marble Bar Chert suggests that they formed deep down in the sea beyond reach of UV radiation. The oxidation to form these crystals could have taken place only by direct combination of Fe^{2+} with abundant oxygen present in the deep ocean water¹⁰. Perhaps the conversion of the deep sea from an anoxic to oxic state may either be due to changes in the submarine topography or due to an influx of a large quantity of oxygenated water-mass from the surface zone. Further, if a large quantity of dissolved oxygen was available covering a vast area deep down the sea, there must have been a good exchange of

oxygen between the atmosphere and the sea. This leads to the conclusion that oxygenic photoautotrophs must have been flourishing in the photic zone of the early Archaean oceans and supplied O_2 to the deep waters, at least 700 million years before the GOE¹⁰.

Another recent study⁷ of hematitized Apex Basalt, the younger of the two basalt layers at the MBC site, also discounts the timing of the GOE and considers the hematite in this basalt formed much before 2.76 b.y. ago. A later deformation episode, occurring probably between 2.9 and 2.7 b.y. ago, and subsequent deep erosion exposed the basalt layer to near-surface environment (<200 m depth of the sea). Detailed field and laboratory studies of the hematite in this basalt indicate that O_2 -rich groundwater had percolated through shear zones in the basalts and formed this mineral prior to 2.76 b.y. ago. This leads to the inference that oxygenated surface environments must have existed more than 300 million years before the widely accepted GOE datum line.

The latest geological find from the MBC undoubtedly presents a strong case for oxidation of the seas and land surfaces much earlier than the GOE. At the same time, it is not clear whether the seas were oxygenated randomly in time and exhibited ups and downs throughout the Archaean era¹⁰. These are points that can be sorted by re-examination of global Archaean Fe, Mn deposits, including those in India in Andhra Pradesh and Orissa states. Although a spate of recent studies have indeed generated considerable data to trace the evolution of oxygen at various times in the Archaean and Pro-

terozoic eons, a consensus on the issue has been elusive and has kept the proponents of the two opposing models on this problem firm in their respective views, backed by continuing fresh inputs favouring their respective stand.

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