Late Archean Surface Ocean Oxygenation

Brian Kendall[1], Chris Reinhard[2], Timothy W. Lyons[2], Alan J. Kaufman[3], Ariel D. Anbar[1,4]

[1] School of Earth and Space Exploration, Arizona State University, Tempe, AZ 85287, USA
[2] Department of Earth Sciences, University of California, Riverside, CA 92521, USA
[3] Departments of Geology and Earth System Science Interdisciplinary Center, University of Maryland, College Park, MD 20742, USA
[4] Department of Chemistry and Biochemistry, Arizona State University, Tempe, AZ 85287, USA

Oxygenic photosynthesis must have evolved by 2.45-2.32 Ga, when atmospheric oxygen abundances first rose above 0.001% present atmospheric level (Great Oxidation Event; GOE). Biomarker evidence for a time lag between the evolution of cyanobacterial oxygenic photosynthesis and the GOE continues to be debated. Geochemical signatures from sedimentary rocks (redox-sensitive trace metal abundances, sedimentary Fe geochemistry, and S isotopes) represent an alternative tool for tracing the history of Earth surface oxygenation. Integrated high-resolution chemostratigraphic profiles through the 2.5 Ga Mt. McRae Shale (Pilbara Craton, Western Australia) suggest a 'whiff' of oxygen in the surface environment at least 50 M.y. prior to the GOE. However, the geochemical data from the Mt. McRae Shale does not uniquely constrain the presence or extent of Late Archean ocean oxygenation. Here, we present high-resolution chemostratigraphic profiles from 2.6-2.5 Ga black shales (upper Campbellrand Subgroup, Kaapvaal Craton, South Africa) that provide the earliest direct evidence for an oxygenated ocean water column. On the slope beneath the Campbellrand – Malmani carbonate platform (Nauga Formation), a mildly oxygenated water column (highly reactive iron to total iron ratios [Fe_{HR}/Fe_T] ≤ 0.4) was underlain by oxidizing sediments (low Re and Mo abundances) or mildly reducing sediments (high Re but low Mo abundances). After drowning of the carbonate platform (Klein Naute Formation), the local bottom waters became anoxic ($Fe_{HR}/Fe_T > 0.4$) and intermittently sulphidic (pyrite iron to highly reactive iron ratios [Fe_{PY}/Fe_{HR}] > 0.8), conducive to enrichment of both Re and Mo in sediments, followed by anoxic and Fe^{2+}-rich (ferruginous)

conditions (high Fe_T, Fe_{PY}/Fe_{HR} near 0). Widespread surface ocean oxygenation is suggested by Re enrichment in the broadly correlative Klein Naute Formation and Mt. McRae Shale, deposited ~1000 km apart in the Griqualand West and Hamersley basins, respectively. Mass independent fractionation of S isotopes ($\Delta^{33}S \neq 0$‰) in the upper Campbellrand Subgroup and Mt. McRae Shale indicates an anoxic atmosphere co-existed with the mildly oxygenated surface ocean. The source of the Re and Mo was likely oxidative subaerial and/or submarine weathering of continental sulphides, which are susceptible to dissolution even if atmospheric pO_2 is at 0.001 to 0.0001% present atmospheric level. Dissolved oxygen in the oceans facilitates transport of Re and Mo as conservative ReO_4^- and MoO_4^{2-} from the site of oxidation to deeper-water, reducing marine sediments. Thus, the geochemical data are consistent with stratified oceans (with oxygenated shallow waters) developing on continental margins more than 100 M.y. prior to the GOE.