# Surface Ocean Oxygenation Preceded the Great Oxidation Event

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Geochemical signatures (redox-sensitive trace metal abundances, sedimentary Fe geochemistry, and S isotopes) from sedimentary rocks provide the tools to elucidate the timing and nature of Earth surface oxygenation. 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). Geochemical data for a "whiff" of oxygen in surface environments at 2.5 Ga (Mt. McRae Shale, Western Australia; Anbar et al. & Kaufman et al. [2007] Science 317, 1900-1906) suggests the evolution of oxygenic photosynthesis preceded atmospheric oxygenation by at least 50 million years. However, the extent of Late Archean surface ocean oxygenation is not known. Here, we present high-resolution chemostratigraphic profiles from 2.6-2.5 Ga black shales (upper Campbellrand Subgroup, 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 [$Fe_{HR}/Fe_T$] $\leq 0.4$) 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. Thus, the geochemical data are consistent with stratified oceans (with oxygenated shallow waters) developing on continental margins more than 100 million years prior to the Great Oxidation Event.