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Paleoproterozoic marine anoxia post-dating the "Great Oxidation Event"

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Several lines of evidence from indicators such as mass-independent sulphur isotope fractionation, Fe-Ti relationships in paleosols, and sediment mineralogy, for example, suggest that atmospheric oxygen levels increased significantly between about 2.4 Ga and 2.2 Ga ago. This is often referred to as the “Great Oxidation Event”. We here focus on Rare Earths and Yttrium (REY) data from 2.6 to 2.2 Ga old iron- and manganese formation, limestone and dolomite from the Transvaal Supergroup, South Africa. The Transvaal Supergroup contains abundant marine chemical sediments that are devoid of detrital aluminosilicates, have experienced only little post-depositional overprint, and hence have recorded the chemical evolution of contemporaneous (shallow) seawater. Regardless of the specific lithology, all marine chemical sediments discussed here display the REY distribution pattern typical of the non-redox-sensitive REY in modern seawater, i.e. the y show enrichment of HREE over LREE, positive anomalies of La and Gd, and super-chondritic Y/Ho ratios. However, the size of the positive Eu anomaly that is indicative of the presence of a high-temperature hydrothermal component in Early Precambrian seawater decreases as the sediments get younger. We emphasize that even the iron- and manganese-formation in the Hotazel Formation does not show any positive Eu anomaly, suggesting that high-temperature hydrothermal REY input had become insignificant. The most interesting feature of the REY distribution is the abundance of Ce relative to its REE neighbours. Cerium anomalies result from the oxidation of Ce(III) to Ce(IV), the subsequent fixation of the latter in compounds with low solubility, and the eventual decoupling of REY(III) and Ce(IV). Hence, the presence of a Ce anomaly in a sediment is evidence for oxic conditions in the Earth’s (near) surface environment. The first chemical sediments in the Transvaal

Supergroup that show Ce anomalies are the manganese-formation in the Hotazel Formation (note that the Hotazel iron-formation does not display Ce anomalies). In marked contrast, the slightly younger Mooidraai limestones and dolomites lack any Ce anomaly. Considering that the Mn-rich sediments from the Hotazel Formation show Ce anomalies (as expected from a Mn-oxide-rich sediment), the absence of Ce anomalies from the younger Mooidraai carbonates indicates the re-establishment of anoxic conditions in the Paleoproterozoic Mooidraai Sea after the postulated Great Oxidation Event. This suggests that the ultimate oxygenation of the Earth's atmosphere-hydrosphere system in the Paleoproterozoic involved a transitional period characterized by transient oxygen-rich environments that became more and more abundant until fully oxic conditions were established in the Late Paleoproterozoic.