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Vanadium and thallium isotope constraints on the global ocean redox state approximately 1.4 billion years ago.

ANDY W HEARD[1], YI WANG[1], CHADLIN M OSTRANDER[1], MAUREEN AURO[1], DON CANFIELD[2], SHUICHANG ZHANG[3], HUAJIAN WANG[4], XIAOMEI WANG[4] AND SUNE GRØNLUND NIELSEN[1]

[1]Woods Hole Oceanographic Institution
[2]University of Southern Denmark
[3]China National Petroleum Corporation
[4]Research Institute of Petroleum Exploration & Development
Presenting Author: andrew.heard@whoi.edu

The oxygenation state of the Mid-Proterozoic (1.8 – 0.8 Ga) ocean and atmosphere is heavily debated and has implications for the relationship between environmental O_2 and the emergence of complex life. While recent geochemical proxy studies of Mesoproterozoic marine sedimentary rocks inform a picture of ocean redox dominated by widespread ferruginous (iron-rich and anoxic) conditions [1], a growing number of datasets indicate that short-lived ocean oxygenation events were recurrent features in this time interval [2–5]. The spatial extent of previously reported Mesoproterozoic oxygen pulses is unclear as they are observed via fundamentally localized environmental proxies. In this study, we report a novel combined application of the vanadium (V) and thallium (Tl) isotope paleoredox proxies to provide a global perspective to this time interval. We reconstructed seawater V ($\delta^{51}V_{SW}$) and Tl ($\varepsilon^{205}Tl_{SW}$) isotopic compositions for shales from Unit 2 of the 1.38-1.39 Ga Xiamaling formation (North China craton) and observed an up-section shift to higher average $\delta^{51}V_{SW}$ values and a short-lived negative perturbation in $\varepsilon^{205}Tl_{SW}$ that are stratigraphically near-coincident. Mass balance models for both isotopic systems are consistent with these isotopic shifts representing an expansion of oxic sedimentary environments from an anoxic (ferruginous) baseline ocean state, with the delayed shift in $\varepsilon^{205}Tl_{SW}$ marking the onset of substantial Mn oxide burial. The long ocean residence time of V and Tl requires that this oxygenation event was regional-to-global in its spatial extent, and may reflect a deepening of the oxycline; either as a purely oceanic phenomenon, or driven by ocean equilibration with a short-lived pulse of atmospheric oxygenation.

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