## Copper-zinc isotopes reveal redox condition driven nutrient cycling in Mesoproterozoic ocean

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It has been suggested that the Mesoproterozoic ocean exhibited heterogeneous oxygenation patterns, characterized by a mix of oxic, ferruginous and euxinia conditions. However, the heterogeneous ocean redox patterns, driving mechanisms and the potential effects on nutrient cycling remain controversial. To further investigate the redox pattern and driving mechanisms of the Mesoproterozoic ocean, we present the first zinc and copper isotope records of black shale of the ~1.46 Ga Hongshuizhuang Formation in Kuancheng, North China, and compare them with redox-sensitive and nutrient elements. The concentrations of redox-sensitive elements at near upper continental crust level are consistent with the turbulent variation of Cu and Zn isotopic compositions in Stage I, with low total organic carbon (TOC) and total sulfur (TS) concentrations, suggesting dynamic suboxic to anoxic conditions. The stable Cu and Zn isotopic compositions, together with higher concentrations of redoxsensitive elements compared to Stage I, indicate an anoxic condition in Stage II. The coupled positive excursion of  $\delta^{65}$ Cu and  $\delta^{66}$ Zn and the increase in total sulfur content during the same interval suggest increased organic carbon burial and the presence of pore-water euxinia in Stage III. Higher TOC, Ba/Al ratios, TOC/P ratios, and lower P/Al ratios in Stage III indicate efficient recycling of phosphorus back into the water column and higher primary productivity levels during this period. It appears that a dynamic redox environment drove nutrient cycling in the Mesoproterozoic ocean, which may have influenced primary productivity and, in turn, affected the redox patterns in the Mesoproterozoic.

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