

## **Phosphate oxygen isotopes of sedimentary apatite from the Mesoproterozoic successions**

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Phosphorus (P) is an essential element for life, and the oceanic P cycle is closely coupled with the global carbon and oxygen cycles via the role of P as a limiting nutrient. Phosphorite as a major sink for P in the ocean is general absent from the Archean Eon and the Mesoproterozoic Era, which have spawned the idea that marine P reservoirs were much smaller when compared with the Neoproterozoic and later. Limited P availability before the Mesoproterozoic is consistent with reconstructions based on P/Fe ratios in iron oxides and low P concentrations in shales. However, other evidence (e.g., measurements of carbonate-associated phosphate) pointed to abundant P in Precambrian oceans. A critical constraint in quantifying the ancient P cycle is a lack of inherent tracer. Since P has only one stable isotope ( $^{31}\text{P}$ ), it cannot be used to monitor P systematics in a similar manner to other essential elements. Alternatively, most P in marine systems is tightly bound to oxygen, permitting the analysis of oxygen stable isotopes as a valuable complement for tracking the P cycle. In this study, we used 1 M HCl to extract phosphate oxygen isotope signals preserved in carbonate fluorapatite (CFA) of the Mesoproterozoic Gaoyuzhuang and Xiamaling Formations, North China. Despite large uncertainties with respect to diagenesis, the derived phosphate oxygen isotopes are significantly lower than those from modern sites with similar depositional depth and latitude, implying a warmer climate during the Mesoproterozoic Era compared to the present day. Based on thermodynamic calculations of saturation state with respect to CFA, we suggest that the elevated temperatures could have hindered P authigenesis, thereby partially accounting for the lack of phosphorite in contemporaneous successions.