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Geochemical Signatures of Paleoproterozoic Oceans: Rare Earth Element and Trace Metal Variations during the 2.5-2.0 Ga Transition

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The 2.5-2.0 Ga period is particularly significant as it marks a transitional phase in Earth's geochemical and biological evolution. During this time, various geochemical proxies, including rare earth elements (REEs) and other key trace elements such as molybdenum (Mo), vanadium (V), and phosphorus (P), provide valuable insights into oceanic and atmospheric conditions, which likely influenced the early development of life and global biogeochemical cycles. However, key questions regarding the link between these elemental changes and environmental evolution remain to be explored. In this study, we present major and trace element data from bulk samples of banded iron formation (BIF), dolomitic marble, and graphite-bearing marble from the early Paleoproterozoic upper Taihua Group, located in the Lushan area on the southern margin of the North China Craton (NCC). The BIF samples exhibit typical characteristics of highly pure marine chemical sediments, including shale-normalized positive La, Ga, and Y anomalies, indicative of a marine depositional setting. These BIF samples also show both negative Ce anomalies and the absence of Ce anomalies, suggesting the presence of both oxic and suboxic/anoxic waters in the ocean. The dolomitic marble samples are characterized by extremely low concentrations of crustal material (such as Al, Ti, Zr, Hf) and high Y/Ho ratios (46-66), further suggesting a purely marine chemical origin. Excluding some contaminated samples, the remaining graphite-bearing marble samples display characteristics similar to those of the dolomitic marble. Both the dolomitic marble and graphite-bearing marble show significant positive Ce anomalies and high light-to-heavy REE ratios (Pr/Yb(SN)), which align closely with the 2.2-2.1 Ga carbonates from the Guanmenshan Formation of the Liaohe Group in the NE Sino-Korean Craton. Combined with the Ce anomalies observed in the BIF samples, these results suggest that seawater during the deposition of the upper Taihua Group was redox-stratified, ranging from oxic shallow waters to deeper anoxic waters. Additionally, the graphite-bearing marble records contemporaneous surface waters that were enriched in nutrients, supporting microbial activity and high productivity. Furthermore, combined with data on Ce and redox-sensitive elements from BIFs worldwide, this suggests a co-evolution of REEs and trace elements with the ocean's redox environments during this period.