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Oceanic nitrate availability during the Proterozoic: insights from the Indian and global deposits

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Nitrate is a key macronutrient essential for the sustenance of primary productivity. Its production and assimilation in the modern day ocean involve multiple enzymatic pathways that involve trace metals such as Mo, Cu, and Fe. The Proterozoic witnessed periods of low (2000 to 1400 Ma) and high (1400 to 800) bio-essential trace metal concentrations in the ocean, which likely regulated nitrate production. To evaluate nitrate availability during fluctuating trace element intervals, we performed a statistical analysis of pre-existing global Proterozoic (offshore) bulk nitrogen isotope ($\boldsymbol{\delta}^{15}N_{bulk}$) data. We also measured $\boldsymbol{\delta}^{15}N_{bulk}$ and redox-sensitive trace metals in the Hindoli (~1800 Ma) and Vindhyan deposits (~1600 to 800 Ma) of Rajasthan, India, to evaluate nutrient dynamics within the Indian basins. Overall, the global analysis showed lower $\boldsymbol{\delta}^{15}N_{bulk}$ during low trace metal interval (2000 to 1400 Ma) compared to Early-Paleoproterozoic, indicating a reduction in nitrate availability. No such conclusive trend could be drawn from low to high trace metal interval (1400 to 800 Ma), due to paucity of global offshore $\boldsymbol{\delta}^{15}N_{bulk}$ data. Our data from offshore deposited Hindoli phyllites and nearshore deposited lower Vindhyan shales, both representative of low trace metal interval (2000 to 1400 Ma) showed relatively lower $\boldsymbol{\delta}^{15}N_{bulk}$, compared to high trace metal interval (1400 to 800 Ma), represented by upper Vindhyan Shales. This suggests relatively lower nitrate availability, in both nearshore and offshore regions, during the low compared to high trace metal interval. Deviations from these observations are possible in basins with regional nitrate oasis and should be explored further. During the high trace metal interval, the Vindhyan basin potentially witnessed variable spatial nitrate availability, with relatively higher availability in nearshore regions (higher $\boldsymbol{\delta}^{15}N_{bulk}$ in Rewa and Bhander groups) and lower availability in offshore regions (lower $\boldsymbol{\delta}^{15}N_{bulk}$ in Bijaygarh Shale ~1210 Ma). This observed gradient could be attributed to relatively increased availability of bio-essential trace elements in the nearshore regions, resulting from their proximity to continental weathering. Overall, our results indicate that nitrate availability in Proterozoic ocean was likely linked to bio-essential trace element availability and their coupled evolution may have played a crucial role in the diversification of eukaryotic life.