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The Geologic Lacustrine Nitrogen Isotope Record Reflects Redox and Alkalinity Changes in the Past 3 Ga

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Nitrogen (N) is an essential component for the building blocks of all life. Studying N cycling throughout Earth's geological history provides us insight into the evolution of life under major biological, tectonic, and geochemical shifts. Taking advantage of the redox sensitivity of N-processes, previous studies have used the N stable isotope composition ($\delta^{15}N$) of ancient marine sediments to reconstruct the N-cycle amidst Earth's oxygenation. Lacustrine $\delta^{15}N$ records, though fewer than marine data, are necessary to develop a global understanding of N-cycling among shifting redox conditions. To determine whether water column redox conditions in lakes affect geochemical signals preserved in the rock record, we compiled N and organic carbon isotope data ($\delta^{15}N$ and $\delta^{13}C_{org}$) from modern anoxic (n = 26) and oxic (n = 155) lakes. We find an average of $\delta^{15}N$: 3.52‰ for modern lake sediments, which is lower than the reported average of 6.7‰ for modern marine sediments. A ~3‰ difference between the two environments suggests major differences in N sources and transformations that are preserved by $\delta^{15}N$ signals. In lakes, there are a few trends that appear related to water column oxygenation. Very negative $\delta^{15}N$ values (i.e. < -5‰) are only found in wholly oxic water columns and very negative $\delta^{13}C_{org}$ (i.e., < -32‰) or very positive (i.e., > -16‰) values belong to sediments from wholly anoxic water columns. These thresholds are linked to anaerobic and aerobic metabolic pathways. To see if these modern isotope trends are consistent in ancient lacustrine sediments, we compiled $\delta^{15}N$ values from 28 stratigraphic units and compared this to the existing marine record. While the marine $\delta^{15}N$ record expresses a high degree of variability through time, the lacustrine $\delta^{15}N$ record reveals a slight increase from the Archean to the Phanerozoic possibly linked to the emergence of new N-metabolic pathways. Extremely positive $\delta^{15}N$ values (> 10‰) in the lacustrine record reveal alkaline lake conditions, further supporting previous use of sediment $\delta^{15}N$ composition as a rough proxy for alkalinity. Terrestrial environments should be further analyzed as they may provide an additional record of past changes in N-cycling that complement marine systems.