

Nitrogen cycling in the Paleoarchean ocean: Isotope records from the Mapepe Formation of the Barberton Greenstone Belt

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Nitrogen is a limiting nutrient for life, and its bioavailability throughout Earth's history is crucial for understanding the biological evolution. However, biogeochemical cycling of nitrogen in the Paleoarchean ocean remains obscure. Here we present organic carbon and nitrogen isotope data for organic matter-rich black shales from the Mapepe Formation of the Fig Tree Group in the Barberton Greenstone Belt, South Africa. The Fig Tree Group consists of 3.28–3.22 Ga marine deposits, and the Mapepe Formation is a unit of clastic and chemical sedimentary rocks including banded iron formation. In the studied section, laminated ferruginous shales and cherts, as well as greenish to black shales, are well-exposed. In black shale samples from the studied section, iron primarily occurs as iron oxides and aluminosilicates. Bulk nitrogen isotope compositions of the studied black shales are heavier than +2‰, and an episodic increase of $\delta^{15}\text{N}_{\text{bulk}}$ values is observed. Notably, those black shale samples with high $\delta^{15}\text{N}_{\text{bulk}}$ values also display relatively low $\delta^{13}\text{C}_{\text{org}}$, high TOC, and positive $\delta^{15}\text{N}_{\text{kerogen}}$ values. This geochemical signature resembles that observed in the *ca.* 2.5 Ga Mt. McRae Formation, which records oxygen oases before the Great Oxidation Event. The positive nitrogen isotope values of our samples suggest development of a ^{15}N -enriched nitrogen pool in the Paleoarchean ocean. Denitrification and anammox are the most common pathway to remove ^{14}N from the reservoir in oxygenated oceans with a large nitrate pool. However, the Archean ocean is generally considered to have been dominantly anoxic, even at the surface, and no data suggests development of oxic conditions. In this case, nitrogen was likely present as ammonium rather than nitrate. If true, partial ammonium oxidation coupled with reduction of iron oxides seems a plausible mechanism for development of a ^{15}N -enriched ammonium reservoir. Iron was likely oxidized above the iron redoxcline, which was followed by iron reduction coupled with oxidation of ammonium, methane, and organic matter below the iron redoxcline. The observed covariation between $\delta^{13}\text{C}_{\text{org}}$ and $\delta^{15}\text{N}_{\text{bulk}}$ values potentially represents an interplay between iron, carbon and nitrogen cycling in the 3.2 Ga ocean.