

Neoproterozoic nitrogen isotope variability associated with the upwelling of hydrothermal ammonium on the submerged Zimbabwe proto-craton

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Unusually negative nitrogen (N) isotope values in shales of the ~2.75 Ga Manjeri Formation (Zimbabwe Craton) suggest the establishment of a deep-water ammonium reservoir that was in excess of the local biological need due to the partial assimilation of ammonium into biomass, some few hundred million years before the aerobic N cycling following the Great Oxidation Event (GOE). The association of these units with extensive submarine volcanism on the submerged Zimbabwe proto-craton may suggest a hydrothermal origin for this deep ammonium reservoir; however, the search for the corresponding positive N isotope reservoir remains elusive and details regarding marine N cycling in a pre-GOE world remain scarce. Thus, here we investigate the N isotope composition of shallow marine carbonate facies of the Manjeri Formation and overlying Cheshire Formation in the Belingwe and Bulawayo greenstone belts. We also utilise the uranium-isotope and cerium-anomaly redox proxies to assess redox conditions in the photic zone. We show that carbonates at these localities are associated with highly elevated bulk $\delta^{15}\text{N}$ values ranging from ca. +20‰ to +40‰. When combined with previously reported negative $\delta^{15}\text{N}$ values from deep-water shales, these values may be explained by the upwelling of ammonium- and ^{15}N -rich waters. Uranium isotope values between ca. -0.3 and -0.6‰ and an absence of cerium anomalies suggest that the depositional environment was anoxic but the local redox potential was sufficiently high to oxidise uranium. Overall, we infer that the shallow marine biosphere on the submerged Zimbabwe proto-craton thrived in an anoxic environment replete with ammonium sourced from the upwelling of hydrothermally influenced waters from the deep basin.