Nitrogen Isotope Evidence for Stepwise Oxygenation of the Ocean during the Great Oxidation Event

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The Earth's atmosphere and oceans experienced a dramatic change in redox conditions during the Great Oxidation Event (GOE), some time between 2.45 and 2.2 Ga ago. This redox transition has modified geochemical cycles of many elements and shaped the environment for subsequent life diversification. However, the precise timing and evolution of oxygenation, as well as the relationships with glaciogenic events and the extent of primary productivity are still debated. In order to constrain the evolution of the redox conditions during the GOE, we analyzed bulk N content and isotope composition in two sedimentary drill cores (TCDP-2 and TCDP-3) recovered from the Turee Creek Group, Hamersley Basin in Western Australia. Major and trace elements as well as organic carbon content and isotope composition were measured on the same samples to get further insight into N biogeochemical cycle. TCDP-2 core samples the Kungarra Fm., which consists of clastic sedimentary rocks overlained by the glaciogenic Meteorite Bore Member deposited ~2.31 Ga ago (Philippot et al., this session). TCDP-3 core containing from bottom to top shales and stromatolitic carbonates of the Kazput Fm., deposited between ~2.31-2.20 Ga.

Bulk N content is remarkably low, and varies from 13.5 to 56.7 ppm (avg = 34.3 ± 12 ppm, n = 11), and 15.7 to 53.4 ppm (avg = 32.4 ± 11.9 ppm, n = 13) in Kungarra and Kazput Fm., respectively. Correlations between N and K or Al contents suggest that N occurs mainly as NH_4^+ substituting for K^+ in clay minerals. The low N content, relative to modern sediments, indicates that the flux of organic matter was low (at least 10 to 100 times less than modern values). $\delta^{15}N$ shows a bimodal distribution, with a range of −0.8 to +4.3‰ (avg = +2.6 ± 1.8‰, n = 11) for the Kungarra Fm. and +6.8 to +11.5‰ (avg = +8.8 ± 1.3‰, n = 13) in the overlying Kazput Fm.. This shift to highly positive $\delta^{15}N$ values likely reflects the expansion of a dissolved nitrate (NO_3^-) reservoir affected by significant denitrification. Thus, N isotopes support post-glacial O_2 production, and NO_3^- formation and accumulation in marine environments between ~2.3 and 2.25 Ga.