Validating a conceptual model of Precambrian N-cycle: Insight from the Dziani Dzaha lake

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Our understanding of the evolution of the biogeochemical N-cycle through times relies heavily on both the precision with which the $\delta^{15}N$ sedimentary rock record is documented and on our ability to interpret it. While the Precambrian $\delta^{15}N$ database is rapidly growing, their interperation remains poorly constrained, especially in the 2.7 to 0.5 Ga time period, which displays a range of $\delta^{15}N$ values mostly positive and comparable to surface sediments in the modern ocean. This range is compatible with various types N-cycles, in which the main processes responsible for $\delta^{15}N$ increase could either be the non-quantitative reduction of NO_3^- to N_2O/N_2 (denitrification) or the non-quantitative oxidation of NH_4^+ to N_2O/N_2 (see review in Ader et al., 2016). The denitrification hypothesis implies significant oxygenation within the water column allowing NO_3^- to accumulate, whereas the ammonium oxidation hypothesis implies a widely anoxic water column where NH_4^+ accumulates. This later conceptual N-cycle model is currently lacking support from modern analogues.

We propose here that the volcanic crater lake Dziani Dzaha (Mayotte, Indian Ocean) might be an interesting candidate. It presents an unprecedented combination of analogies with Proterozoic environments including: primary productivity massively dominated by cyanobacteria; permanently anoxic conditions at shallow depth in spite of seasonal mixing; NO_3^- content below detection limit; accumulation of NH_4^+ at depth during the stratified season. It is worth noting however, that its pH value of 9.2 is probably not analoguous to proterozoic oceans, except for alkaline lakes and restricted basins. In this lake, the $\delta^{15}N$ values of primary producers range from 6 to 9‰ and are recorded with a positive offset in the sediments ($9<\delta^{15}N<13$‰). Because N-sources to the system present $\delta^{15}N$ values below 7‰, ^{14}N-enriched nitrogen must escape from the lake. NO_3^- contents being below detection limit, the main pathway envisaged for this N-loss is NH_4^+ oxidation to N_2O/N_2, although it is not possible yet to confidently exclude NH_3 degassing. If confirmed, this would provide strong support for the hypothesis that positive $\delta^{15}N$ values in Precambrian rocks may indicate dominantly anoxic oceans, devoid of NO_3^-, in which NH_4^+ is non-quantitatively oxidized to N_2/N_2O.