Millimolar concentrations of bioavailable ammonium in hydrothermal fluids: Evidence from altered basalts in the Paleoproterozoic Zaonega Formation, NW Russia

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In the modern ocean, 99% of nutrients are recycled through aerobic respiration of biomass within the water column. In the Precambrian, when conditions were largely anoxic, this oxidative recycling process was suppressed, limiting the re-supply of nutrients to primary producers. In volcanically active basins, hydrothermal fluid circulation through sedimentary packages may have acted as an alternative mechanism that liberated nutrients from buried sediments and dispersed them back into the water column. Support for this hypothesis has been documented from Archean and Proterozoic strata; however, the magnitude of this recycling flux has not previously been quantified. Here we present data from the Paleoproterozoic Zaonega Formation (2.0 Ga) in NW Russia, where hydrothermally altered basalts are interbedded with organic-rich sedimentary strata. The altered basalts show enrichments in nitrogen of up to 0.6 wt.% compared to a few ppm in unaltered equivalents. These enrichments are likely in the form of ammonium hosted in secondary potassic phyllosilicate minerals. Assuming that these minerals assimilated ammonium at equilibrium from the fluid suggests dissolved ammonium concentrations in the millimolar range, comparable to modern sediment-hosted hydrothermal vents. Previously reported isotopic offsets of approximately 10 ‰ between organic-bound and silicate-bound nitrogen in interbedded sedimentary strata likely reflect by partial biological uptake of ammonium from the vent fluid. Our results suggest that hydrothermal nutrient recycling on the anoxic early Earth may have created local hotspots of biological productivity. Submarine volcanism was thus perhaps an important mechanism for sustaining a rich biosphere. Lastly, altered igneous rocks can be used as a recorder of this recycling flux.