

Abiotic Formation and Fate of Ammonium in the Hadean Ocean

Alexander Smirnov
Department of Geosciences
Stony Brook University
Stony Brook, NY 11794-2100
USA
asmirnov@ic.sunysb.edu

Nicholas J. Tosca, Martin A.A. Schoonen
Department of Geosciences
Stony Brook University
Stony Brook, NY 11794-2100
USA

Devicharan Chidambaram, Gary Halada
Material Science Department
Stony Brook University
Stony Brook, NY 11794-2100
USA

Branislav _upták
Geological Institute
Slovak Academy of Sciences
Bratislava, 84505
Slovakia

$\text{NH}_3/\text{NH}_4^+$ are precursors for prebiotic synthesis reactions of complex organic molecules such as amino acids. In a N_2 -dominated, mildly reducing Hadean atmosphere, non-atmospheric sources of $\text{NH}_3/\text{NH}_4^+$ must have been present and utilized in prebiotic synthesis. N_2 reduction is kinetically inhibited due to its strong triple bond but the reaction may be promoted by mineral surfaces. Here we present our research into the formation and fate of NH_4^+ in the Hadean ocean – including NH_4^+ formation and sequestration in the rocks and minerals of the ocean floor. Based on our experimental results we envision the following scenario: During the dissolution of Ni-containing olivine at hydrothermal conditions Ni and Fe are mobilized, reduced and deposited as Ni-Fe alloys or sulfides depending on sulfur fugacity of the system. Such alloys/sulfides are regularly present in submarine hydrothermal (axial) or serpentinization-driven (off-axis) systems, albeit not in great quantities. Our research shows that such $\text{Ni}_x\text{Fe}_{1-x}$ alloys are effective in reduction of N_2 to NH_4^+ at hydrothermal conditions, possibly through surface-mediated catalysis. By definition the catalyst does not change and thus a small amount of alloy can catalyze the formation of large amounts of NH_4^+ . Once produced, NH_4^+ can be immobilized through surface sorption on rocks and minerals such as mica, plagioclase, pyroxenite, peridotite and diabase. However, as the ionic strength of the seawater increases other cations outcompete NH_4^+ for sorption sites. Consequently, dissolved NH_4^+ would have been available for synthesis reactions in seawater at moderate to high ionic strength.