Abiotic Nitrogen reduction in Hadean hydrothermal systems

A. SMIRNOV[1,2], D. HAUSNER[3], R. LAFFERS[1], F. M. MCCUBBIN[1], D.R. STRONGIN[3], AND M.A.A. SCHOONEN[1]

[1]Department of Geosciences, SUNY Stony Brook, Stony Brook, NY 11794, USA (asmirnov@gl.ciw.edu)
[2]Geophysical Laboratory, 5251 Broad Branch Road, NW, Washington, DC 20015, USA
[3]Department of Chemistry, Temple University, PA 19122, USA

One of the outstanding questions in Astrobiology is the source and formation mechanisms of NH_4^+ which presumably was required for reactions of prebiotic synthesis and origin of life. The uncatalyzed reduction of abundant N_2 to NH_4^+ is prohibitively slow due to the strong triple bond in the molecule. However, NO_3^- and NO_2^- present in the Hadean Ocean as result of atmospheric reactions may have been more susceptible to reduction. We have experimentally tested the hypothesis, which suggests that Ni, Fe metals and alloys formed as a result of hydrothermal (HT) serpentinization processes in the Hadean oceanic crust could have acted as catalysts and/or reactants in reactions leading to abiotic NH_4^+.

Our results show NO_3^- and NO_2^- were converted into NH_4^+ more rapidly than N_2, and the reduction process had a strong temperature dependence. Metals, especially Ni were found to be more effective than alloys in reducing N_2 with yields usually not exceeding few percent. Based on the experimental results we have estimated NH_4^+ yield of Hadean HT systems from to be approximately 10^{10}-10^{12} mol.yr^{-1} which is comparable to values estimated by Brandes *et al*, 1999 (10^{10}-10^{11} mol.yr^{-1}) and Schoonen and Xu (2001) (10^8-10^9 mol.yr^{-1}) in HT systems as well as Summers and Chang (1993) for NO_2^- reduction by Fe^{2+}. Our estimate only includes N_2 to NH_4^+ reaction yield and therefore if NO_2^-/NO_3^- were present in the advected seawater, the yields would have been proportionally higher considering their high conversion rates to NH_4^+ in the presence of metals/alloys.

We have also considered iron meteorites as possible sources of N since they commonly cointain reduced N species such as nitride (N^{3-}) which could have reacted to form NH_4^+ during dissolution in the Hadean Ocean. When compared, however, with HT production, the meteoritic NH_4^+ flux during the Late Heavy Bombardment is approximately 6 orders of magnitude smaller.

References

Brandes, J.A., Boctor, N.Z., Cody, G.D., Cooper, B.A., Hazen, R.M. and Yoder, H.S. (1998), Abiotic nitrogen reduction on the early Earth. *Nature* **395**, 365-367.

Schoonen, M.A.A. and Xu, Y. (2001), Nitrogen reduction under hydrothermal vent conditions: Implications for the prebiotic synthesis of C-H-O-N compounds. *Astrobiology* **1**, 133-141.

Summers, D.P. and Chang, S. (1993), Prebiotic ammonia from reduction of nitrite by iron(II) on the early Earth. *Nature* **365**, 630-632.

Melt segregation and near source fractionation: Examples from small scale basaltic systems

IAN E M SMITH

Geology programme, School of Geography, Geology and Environmental Sciences, University of Auckland, New Zealand (ie.smith@auckland.ac.nz)

Basaltic magmatic systems, expressed at the earth's surface as volcano fields, are characterised by very low rates of magma production (< 1.0^{-4} km^3 /year) over relatively long time scales (up to 10^7 years); these are tiny igneous provinces contrasting with Large Igneous Provinces that represent the other extreme in the spectrum of mantle derived magmatism. Tiny igneous provinces are the result of very small degrees of partial melting from a mantle source. In the Auckland volcanic field of Northern New Zealand, sampling of stratigraphically defined eruption sequences typically shows compositional trends in small magma batches that cannot be accounted for by fractionation involving low pressure mineral assemblages in a shallow pre-eruption environment. Detailed study of several individual volcanic centres in the Auckland field has defined two styles of compositional variation. 1). Least evolved compositions (as defined by geochemical parameters such as Mg-number and incompatible element content) are erupted first followed by more eveolved compositions. This is interpreted to reflect magma extraction from a source in which a thermal gradient has produced a range of melting proportions with the greater proportion melt leading the extraction process. 2). The eruption sequence is initiated by relatively evolved compositions followed sequentially by progressively less evolved compositions. This trend is interpreted as the result of high pressure fractionation immediately above the source in a part of the conduit where melt is thermally connected to its surroundings and side wall crystallisation controls fractionation. The fact that these well defined compositional variations can be observed in stratigraphic sequence shows that the fractionated magma column rose very rapidly and without mixing once it left the source region. Further, such subtle compositional trends are probably only preserved because of the extremely small volumes of melt involved. In the Auckland volcanic field there is evidence for these extraction/fractionation processes occuring in both garnet and spinel peridotite facies giving rise to a range of alkaline to sub-alkaline basalt compositions. There is also evidence for compositionally distinct small magma batches coexisting independantly and rising simultaneously to the surface demonstrating the inherent instability of small scale mantle based magmatic systems.