NITROGEN CONCENTRATIONS AND ISOTOPIC COMPOSITIONS OF ALTERED TERRESTRIAL GLASSY BASALTIC ROCKS, AND IMPLICATIONS FOR ASTROBIOLOGY

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Introduction: Multiple complementary lines of evidence demonstrate that microbial life rapidly colonizes subaqueously-emplaced terrestrial glassy basaltic rocks [1-5]. Evidence for the microbial alteration of such rocks has been reported from modern ocean crust, ophiolites, and Archean greenstone belts extending to ~3.5 Ga [1-5]. Altered glassy basaltic rocks have the potential to retain a variety of signatures of past biological activity including microbial alteration textures (ichnofossils), element distributions, organic compounds, and isotopic compositions [1-5]. Here we report on the N contents and isotopic compositions of modern and ancient terrestrial subaqueous basaltic rocks, discuss the biotic and abiotic processes generating these terrestrial N signatures, and briefly speculate regarding implications for the preservation of isotopic biosignatures in extraterrestrial materials.

Modern N contents and isotopic compositions: Nitrogen isotope data from modern oceanic crust samples suggest that microbial N-isotope biosignatures may also be preserved. Basaltic whole-rocks and separates of variably palagonitized volcanic glass, from the modern seafloor, are enriched in N (whole-rocks and glasses up to 18.2 ppm, unpublished data) and have elevated $\delta^{15}N_{air}$ (up to +8.3‰) relative to that of fresh MORB (the latter near -5‰). The N signatures identified in this work are consistent with the addition of sedimentary/organic N via interaction with pore fluids, with or without direct mediation by biological activity. Marine sedimentary NH_4^+, which is bound in K^+ sites of clay minerals during basaltic alteration due to its similar size and charge, is partially produced from mineralized organic material (OM) that carries its isotopic signature without further fractionation during the conversion [6]. Marine OM is enriched in ^{15}N due to the process of denitrification (biologic conversion of NO_3^- to N_2), which favors ^{14}N for the gaseous phase and leaves ^{15}N-enriched NO_3^- to be reincorporated into OM. Any enrichments of ^{15}N in altered basalts from the expected mantle-like MORB value indicate biological activity and a basin-wide (if not global) biological N cycle. Even if no *in situ*, penecontemporaneous biological activity was present in the altered glass; the existence of an enriched ^{15}N reservoir may constitute global evidence for biological activity.

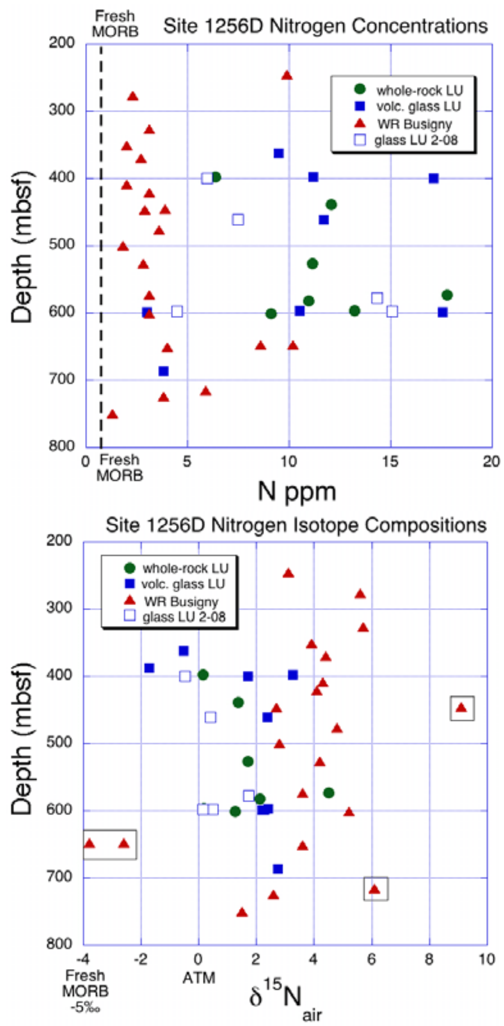

Figure 1: Nitrogen concentrations (top) and isotopic compositions (bottom) of whole-rock samples and separated glassy material from modern seafloor basalt. Note the large shifts in both concentration and $\delta^{15}N$ relative to fresh MORB (< 2 ppm, -5‰, respectively). Also included are data from Busigny et al. [6], for comparison.

Ancient N contents and isotopic compositions: Nitrogen isotope analyses of ancient altered basaltic rocks are not common, but ca. 2.7 Ga proto-glassy lavas altered to greenschist-facies exhibit similar enrichments in N content and $\delta^{15}N_{air}$ relative to MORB. Whole-rock analyses of both putative ichnofossil-bearing and non-ichnofossil-bearing samples demonstrate mostly positive $\delta^{15}N_{air}$ up to +6.9‰ (Fig. 2). Most of the whole-rock samples from massive and proto-glassy flow units fall within the range for Late Archean kerogens (-6 to +12‰), which represent organic N that escaped mineralization in marine sediments [8-11]. Again, the enrichment of ^{15}N in the Archean basaltic rocks demonstrates alteration by sedimentary/organic N-rich fluids carrying $\delta^{15}N_{air}$ signatures representative of OM. The putative ichnofossil-bearing samples appear not to host N isotope signatures representative of chemolithoautotrophic biomass, but it is likely that very little biomass remains in the tubular structures to produce any substantial signal. The whole-rock N isotopes of the Archean basaltic rocks demonstrate the existence of marine N fractionation due to biologic denitrification.

Implications for Mars: Mars has a mantle $\delta^{15}N_{air}$ of ~-30‰ [12-14], and the Martian atmosphere (measured by the Viking landers) has $\delta^{15}N_{air}$ of ~-620 ± 160‰ [15-16], Mars atmosphere N in Martian meteorites including EET 79001 and ALHA 84001 range from $\delta^{15}N_{air}$ of ~300-400 ‰ [12-14]. While there is a large variability in Martian atmospheric N isotopic composition, both Martian mantle and atmosphere have negative values. The presence in Martian meteorites of a nitrogen component with $\delta^{15}N_{air}$ ~-20‰ [e.g., 17] points to a need for more detailed, component-specific study of Martian samples to determine whether this N reflects Martian processes similar or analogous to those occurring on Earth. Basaltic rocks are widely distributed in the solar system, notably on Mars, where there is substantial evidence for water-basalt interaction over geologic timescales [18].

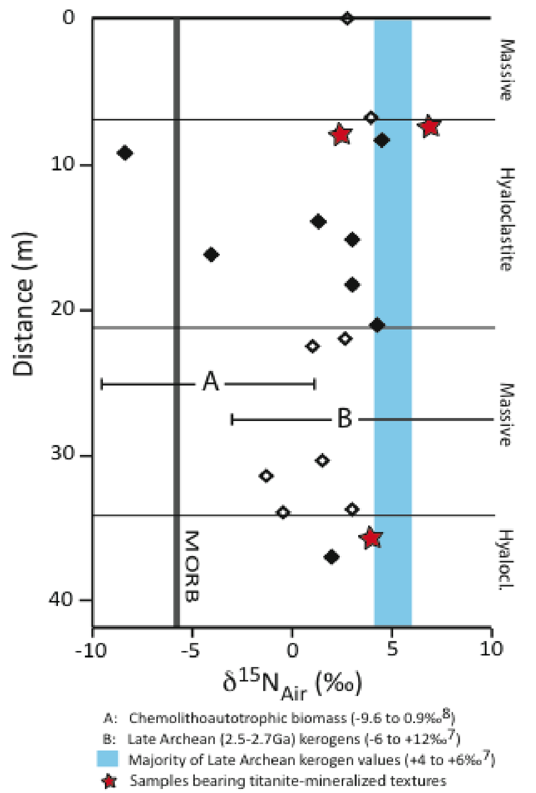

Figure 2: N isotope compositions for variably altered samples collected from a section of alternating hyaloclastite and massive flows from ca. 2701 Ma altered basaltic andesites of the Blake River Group in the Abitibi greenstone belt [11].

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