ISOTOPIC COMPOSITIONS AND MINERAL RESIDENCY OF NITROGEN IN ALTERED TERRESTRIAL GLASSY BASALTIC ROCKS: IMPLICATIONS FOR ASTROBIOLOGY

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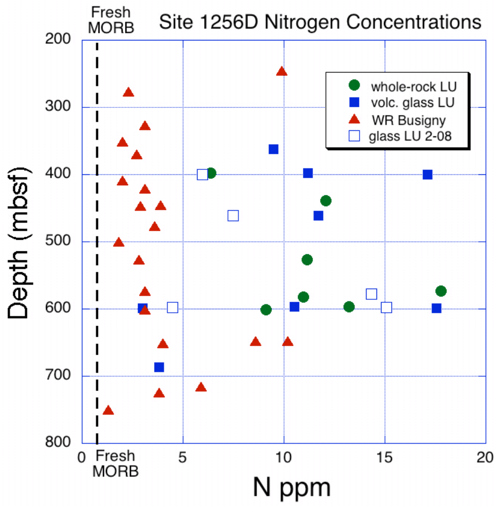
Introduction: Palagonitized basaltic glasses on the modern seafloor (ODP Site 1256) contain 3-18 ppm N with $\delta^{15}N_{air}$ of up to +7‰. Variably-altered glasses in Mesozoic ophiolites (Troodos, Cyprus; Stonyford Volcanics, California) contain 2-33 ppm N with $\delta^{15}N$ of -5.7 to +7‰. All altered glasses have N contents higher than those of fresh MORB glass (<2 ppm), reflecting N enrichment, and most of the glasses have $\delta^{15}N$ higher than that of unaltered MORB (-5±2‰). Glass from the two Mesozoic ophiolite sites contains textural evidence for microbial activity in the form of microtubules [1-4] but the contribution of microbial activity to the N enrichment and elevated $\delta^{15}N$ remains uncertain. Phyllosilicates and possibly also zeolites are likely mineral hosts for the N in these glasses, likely largely as NH_4^+ in clay minerals (2:1 phyllosilicates smectite and illite).

Volcanic glasses from the modern seafloor (ODP Site 1256): Basaltic whole-rocks and separates of variably palagonitized glass from Site 1256 are enriched in N (up to 18.2 ppm) and have elevated $\delta^{15}N_{air}$ (up to +8.3‰) relative to fresh MORB (**Fig. 1**). These signatures are consistent with addition of sedimentary-organic N via pore fluid, with or without direct biological mediation. Marine sedimentary NH_4^+, bound in K^+ sites of clay minerals during diagenesis, is partly produced through mineralization of organic material (OM) and these clays appear to inherit the organic isotopic signatures with little fractionation during incorporation [5]. Microbial conversion of NO_3^- to N_2 (denitrification) produces ^{15}N-enriched NO_3^- and this fractionated N can be incorporated into OM and, with conversion to NH_4^+, into clays [6]. Shifts in the $\delta^{15}N$ of altered basalts, toward higher/positive values can serve as records of this set of processes. Circulating hydrothermal fluids could leach NH_4^+ from nearby sediments then fix this NH_4^+ into the extremely chemically reactive volcanic glasses during palagonitization [6,7].

Mesozoic volcanic glasses: Variably-altered volcanic glasses from two Mesozoic ophiolite suites show elevated N concentrations and $\delta^{15}N$, relative to MORB, similar to those in glasses from the modern seafloor. Again, the increases in the $\delta^{15}N$ of these basaltic rocks appear to reflect their interaction with fluids containing N from a sedimentary-organic source. Glasses from these ophiolites contain micro-tubules believed to be microbial in origin [1-4,9], but it is likely that very little biomass remains in these structures to produce a substantial N signal.



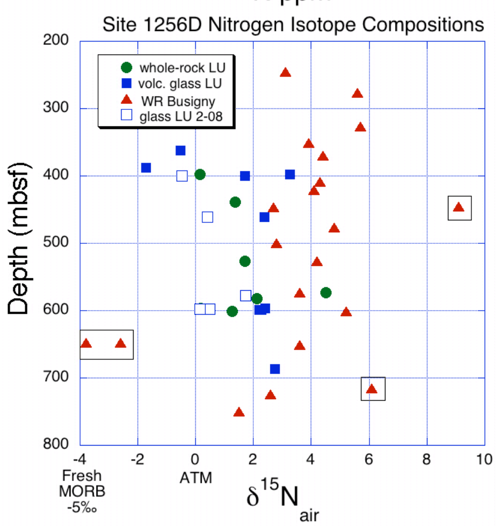


Figure 1: Nitrogen concentrations (top) and $\delta^{15}N$ (bottom) of whole-rock samples and separated glassy material from seafloor basalt on the modern seafloor. Note the large shifts in concentration and $\delta^{15}N$ relative to fresh MORB (< 2 ppm, -5‰). Data from Busigny et al. [6] included for comparison. Few microtubules have been identified in these glasses [8].

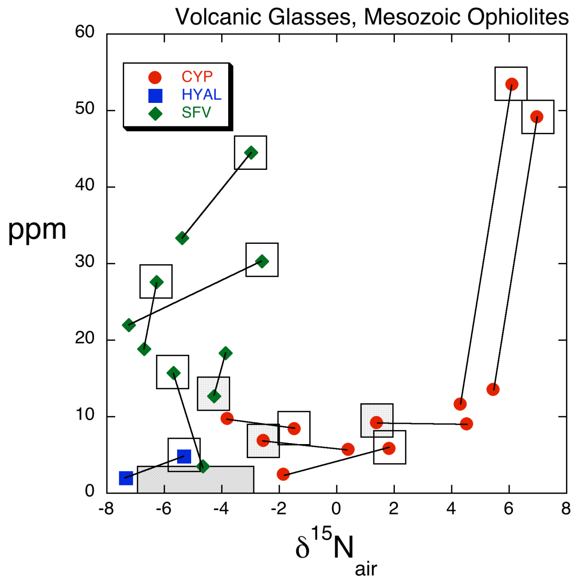
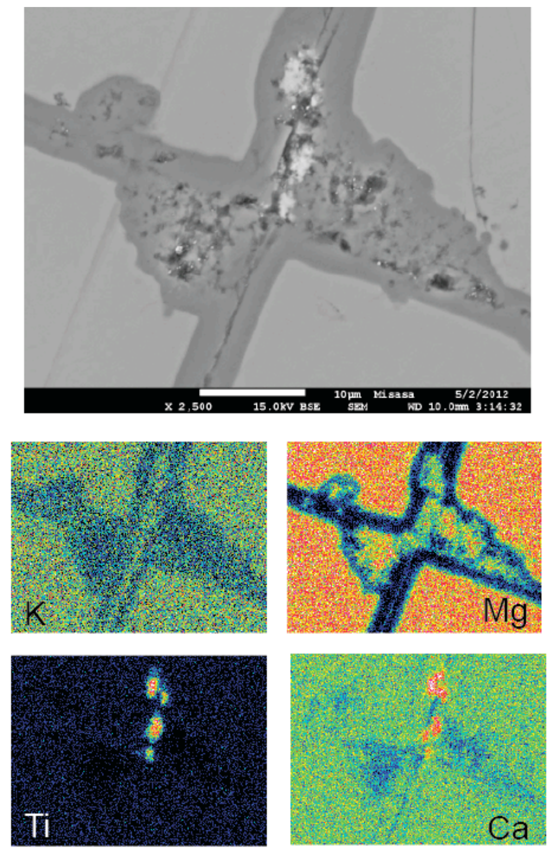


Figure 2 (ABOVE): Nitrogen concentrations and isotopic compositions of variably altered volcanic glasses from Troodos and the SFV - tie lines connect data for less altered (no boxes) and more altered (boxes) glasses from the same samples. Nitrogen in the more altered SFV glasses (up to 45 ppm) has $\delta^{15}N$ near that of fresh MORB (grey region), perhaps indicating the incorporation of N from underlying, degassing lavas and intrusive bodies.

Figure 3 (RIGHT): SEM image and element maps for a fracture junction in an SFV glass sample. Ca-Ti-Si enrichments represent titanite, a common phase in such features. K is depleted in some regions but possibly enriched in the center of the fractures. STEM images of the fractures and microbial tubules confirm the presence of clay minerals (likely smectite and illite; for Troodos, [2-4]).

Imaging and chemical analyses of the altered glasses: A combination of petrographic and chemical analysis and imaging by SEM and STEM indicates the presence of phyllosilicates (smectite, illite) in both the palagonitized cracks and the putative microbial tubules (Fig. 3). K enrichments in some fractures and microtubules, and SEM/STEM imaging, demonstrate the presence of clay minerals, likely smectite and illite capable of housing N as NH_4^+ (also see [2,3]). For Troodos glasses, Wacey et al. [4] confirmed the linings of some microbial tubules with C (± N), providing another possible N contribution to the bulk-glass analyses [cf. 10, 11].

Implications for astrobiology: A number of strategies have been proposed for the search for life on Mars, including work on N cycling based on terrestrial analog sites and materials [12]. The enhanced chemical reactivity of volcanic glass makes it a useful receptacle for biologically processed N, yielding information regarding biogeochemical pathways. Documentation of the enrichment of N in volcanic glass on Earth's modern and ancient seafloor (and the isotopic composition of this N) is relevant to study of modern global N subduction fluxes [6,7] and ancient life on Earth [13]. Altered glasses could similarly serve as valuable tracers of N biogeochemical processing on Mars, and sample return missions should prioritize return of variably palagonitized basaltic rocks and related regolith. Investigation of the silicate N isotope composition of martian meteorites that have experienced aqueous alteration (e.g., Tissint meteorite [12,14]) can also provide insights regarding martian surface N cycles, including their temporal evolution.



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