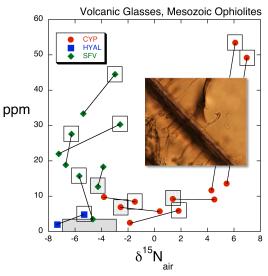
**ENRICHMENT OF SEDIMENTARY/ORGANIC NITROGEN IN ALTERED TERRESTRIAL GLASSY BASALTIC ROCKS: POSSIBLE IMPLICATIONS FOR ASTROBIOLOGY.** G. E. Bebout<sup>1</sup>, N. R. Banerjee<sup>2</sup>, M. R. M. Izawa<sup>2,3</sup>, K. E. Lazzeri<sup>1</sup>, K. Kobayashi<sup>4</sup> & E. Nakamura<sup>4</sup>, <sup>1</sup>Dept. Earth and Environ. Sci., Lehigh Univ., Bethlehem, PA, USA (geb0@lehigh.edu), <sup>2</sup>Dept. Earth Sci., Western Univ., London, ON, Canada, <sup>3</sup>Dept. Natural History, Royal Ontario Museum, Canada, <sup>4</sup>Pheasant Memorial Laboratory, ISEI, Okayama Univ., Misasa, Japan

Introduction: Various strategies have been proposed for the search for life on Mars, including work on N cycling based on terrestrial analog sites and materials [1]. The enhanced chemical reactivity of volcanic glass makes it a useful receptacle for biologically processed N, potentially yielding information regarding biogeochemical pathways. Documentation of N enrichments 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 [2,3] and ancient terrestrial life [4]. Altered glasses could similarly serve as valuable tracers of N (bio)geochemical processing on Mars — sample return missions should prioritize return of palagonitized basaltic rocks and related regolith.

**Observations:** Palagonitized basaltic glasses on the modern seafloor (ODP Site 1256) contain 3-18 ppm N with  $\delta^{15}N_{air}$  of -1.8 to +3.3‰ [5]. Variably-altered glasses in Mesozoic ophiolites (Troodos, Cyprus; Stonyford Volcanics, California) contain 2-55 ppm N with  $\delta^{15}N$  of -7.5 to +7‰ (**Fig. 1**). 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 fresh MORB (-5 ± 2‰). Glass from the ophiolites contains textural evidence for microbial activity in the form of microtubules [6-10] but the contribution of microbial activity to the N enrichment remains uncertain.

Elevated N ppm and  $\delta^{15}$ N of separates of variably palagonitized glass from Site 1256 and the ophiolites (particularly Troodos) are consistent with addition of sedimentary/organic N via pore fluid, with or without direct biological mediation. Marine sedimentary NH<sub>4</sub><sup>+</sup>, bound in K<sup>+</sup> sites of clays 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 [11]. Microbial conversion of NO<sub>3</sub> to N<sub>2</sub> (denitrification) produces <sup>15</sup>N-enriched NO<sub>3</sub> and this fractionated N can then be incorporated into OM and, with conversion to NH<sub>4</sub><sup>+</sup>, into clays. Circulating hydrothermal fluids could leach NH<sub>4</sub><sup>+</sup> from nearby sediments then fix this NH<sub>4</sub><sup>+</sup> into the extremely chemically reactive volcanic glasses during palagonitization.

Petrographic and chemical analyses and imaging by SEM and STEM indicate the presence of phyllosilicates in the palagonitized cracks and putative microbial tubules. Enrichments of  $K^+$  in some fractures and microtubules, and SEM/STEM imaging, demonstrate the presence of clays, likely smectite and illite, capable of housing N as  $NH_4^+$  ([5]; also see [7,8]). For Troodos glasses, Wacey et al. [9] suggested the lining of some microbial tubules with C ( $\pm$  N), providing another possible N contribution to bulk-glass analyses [cf. 12,13].



**Fig. 1.** Nitrogen concentrations and isotopic compositions of variably altered volcanic glasses from Troodos (CYP) and the Stonyford Volcanics (SFV) - tie lines connect data for less altered (no boxes) and more altered (boxes) glasses from the same samples. Inset photo is of an SFV palagonitized fracture (upper left to lower right) with putative microbial tubules emanating from it. SFV glasses have  $\delta^{15}N$  values near those of the upper mantle and unaltered MORB (grey region), perhaps indicating incorporation of N from underlying, degassing lavas and intrusive bodies.

References: [1] M. L. Fogel and A. Steele (2013) *ELEMENTS*, 9, 367-372. [2] V. Busigny et al. (2005), *Gcubed*, 6 (12). [3] L. Li et al. (2007), *GCA*, 71, 2344-2360. [4] L. D. Anderson et al. (2010) *LPSC* Abs. #1668. [5] G. E. Bebout et al. (2014) *LPSC* Abs. #1532. [6] H. Furnes et al. (2001) *Jour. Geol. Soc.*, 158, 75-84. [7] E. Knowles et al. (2013) *EPSL*, 374, 239–250 [8] D. Fliegel et al. (2012) *GCA*, 96, 80-93 [9] Wacey et al. (2014) *Chem. Geol.*, 363, 1-12. [10] C. M. Santelli et al. (2010) *Geomicrobiol. Jour.*, 27, 2, 158-169. [11] S. R. Boyd (2001) *Chem. Geol.*, 176, 1-30. [12] N. McLoughlin et al. (2011) *Chem. Geol.*, 289, 154-162. [13] T. Torsvik et al, (1998) *EPSL*, 162, 165-17.