Nitrogen Concentrations and Isotopic Compositions of Seafloor-Altered Terrestrial Basaltic Glass: Implications for Astrobiology

G.E. Bebout,^{1,2} N.R. Banerjee,³ M.R.M. Izawa,^{2,3} K. Kobayashi,² K. Lazzeri,¹ L.A. Ranieri,¹ and E. Nakamura²

Abstract

Observed enrichments of N (and the $\delta^{15}\text{N}$ of this N) in volcanic glasses altered on Earth's modern and ancient seafloor are relevant in considerations of modern global N subduction fluxes and ancient life on Earth, and similarly altered glasses on Mars and other extraterrestrial bodies could serve as valuable tracers of biogeochemical processes. Palagonitized glasses and whole-rock samples of volcanic rocks on the modern seafloor (ODP Site 1256D) contain 3–18 ppm N with $\delta^{15}\text{N}_{\text{air}}$ values of up to +4.5‰. Variably altered glasses from Mesozoic ophiolites (Troodos, Cyprus; Stonyford volcanics, USA) contain 2–53 ppm N with $\delta^{15}\text{N}$ of –6.3 to +7‰. All of the more altered glasses have N concentrations higher than those of fresh volcanic glass (for MORB, <2 ppm N), reflecting significant N enrichment, and most of the altered glasses have $\delta^{15}\text{N}$ considerably higher than that of their unaltered glass equivalents (for MORB, $-5 \pm 2\text{‰}$). Circulation of hydrothermal fluids, in part induced by nearby spreading-center magmatism, could have leached NH_4^+ from sediments then fixed this NH_4^+ in altering volcanic glasses. Glasses from each site contain possible textural evidence for microbial activity in the form of microtubules, but any role of microbes in producing the N enrichments and elevated $\delta^{15}\text{N}$ remains uncertain. Petrographic analysis, and imaging and chemical analyses by scanning electron microscopy and scanning transmission electron microscopy, indicate the presence of phyllosilicates (smectite, illite) in both the palagonitized cracks and the microtubules. These phyllosilicates (particularly illite), and possibly also zeolites, are the likely hosts for N in these glasses. Key Words: Nitrogen—Nitrogen isotope—Palagonite—Volcanic glass—Mars. *Astrobiology* 18, 330–342.

1. Introduction

NITROGEN IS AN ESSENTIAL element for all living organisms and is central in the structure of amino acids, proteins, nucleic acids, and other substances vital to life. Living organisms process initially atmospheric N that can then be incorporated into mineral phases and conveyed into the rock record (see Bebout *et al.*, 2013). The association of N with life on Earth makes it a compelling element for consideration in our search for life elsewhere in our solar system (Capone *et al.*, 2006; see Fogel and Steele, 2013). Strongly depending upon redox conditions, N can exist in several important molecules other than N_2 , including NH_4^+ (ammonium), NH_3 (ammonia), and NO_3^- (nitrate), increasing its reactivity in both biotic and abiotic settings and producing significant stable isotope fractionation (Busigny and Bebout, 2013; Li

et al., 2014; Zerkle and Mikhail, 2017). This chemical reactivity can result in the long-term storage of N in a variety of mineral phases but principally in silicates, sulfates, and nitrates (see Holloway and Dahlgren, 2002; Bebout *et al.*, 2015; Johnson and Goldblatt, 2015; Lazzeri *et al.*, 2017).

The low atmospheric concentration of N_2 on Mars (1.9 mol %; Mahaffy *et al.*, 2013) has driven debate regarding the “missing” N, which could have escaped to space (explaining the observed enrichment in the heavier isotope, ^{15}N , in the residual atmosphere; Aoudjehane *et al.*, 2012; Wong *et al.*, 2013) or could have been buried in the regolith (dust, soil, and broken rock at the martian surface; Manning *et al.*, 2008). Mancinelli and Banin (2003) hypothesized that typical martian soils may resemble desert soils on Earth and are likely to contain N as nitrate or as NH_4^+ bound in aluminosilicate minerals. Several groups have been studying N cycling in the

¹Department of Earth and Environmental Sciences, Lehigh University, Bethlehem, Pennsylvania, USA.

²Pheasant Memorial Laboratory for Geochemistry and Cosmochemistry, Institute for Planetary Materials, Okayama University, Misasa, Japan.

³Department of Earth Sciences, Western University, London, Canada.

Mars analog environments of dry, arctic areas (*e.g.*, Starke *et al.*, 2013) and gypsum sand dunes (*e.g.*, Glamoclija *et al.*, 2012).

A number of minerals (and rocks) common on Earth, that could potentially house N, are likely to be present and possibly abundant on the martian surface, based either on recent satellite spectral studies or predicted theoretically as products of hydrothermal alteration in and around martian volcanic centers or impact craters (see Osinski *et al.*, 2013; recent review of martian surface mineralogy by Ehlmann and Edwards, 2014). However, lacking at present is a full survey of the specific mineral phases in which N could reside and the degree to which these minerals are capable of preserving isotopic records of biogeochemical processes occurring at the time of their crystallization. Recent spectral analysis of the martian surface has revealed an abundance of hydrated phases, perhaps including zeolite and clay minerals (Bish *et al.*, 2003; Mancinelli and Banin, 2003; Ruff, 2004; Newsom, 2005; Poulet *et al.*, 2005; Janchen *et al.*, 2006; Wyatt and McSween, 2006; Ehlmann and Edwards, 2014), raising questions regarding the significance of these phases for surface/near-surface storage of H₂O and possibly also any biologically processed molecules such as CH₄, NH₄⁺, NO_x, and N₂ (Fogel and Steele, 2013). There has been speculation that zeolites and clays could occur on Mars both as alteration products in volcanic glass (in both intact basaltic rocks and immature sandstones containing volcanic grains; see Cannon *et al.*, 2015a) and as cement in sandstones (Basu *et al.*, 1998; Towell and Basu, 1999; Chan *et al.*, 2005). These minerals, along with sulfates and possibly also halides, could incorporate and store atmospheric/organic nitrogen as N₂ or NH₄⁺ (see Mancinelli and Banin, 2003). New SAM/MSL results indicate “biochemically accessible” N (as nitrate) in scooped eolian sediment and drilled mudstone (Stern *et al.*, 2015; discussion of surface nitrate cycling by Manning *et al.*, 2008). Phyllosilicate-bearing alteration assemblages, almost certainly of martian origin, have been documented in several martian meteorites including Nahkla (Fisk *et al.*, 2006; Lee *et al.*, 2013) and NWA 817 (Gillet *et al.*, 2002). Carbonates, sulfates, halides, and other products of aqueous alteration that could host N have been observed in numerous martian meteorites (*e.g.*, Bridges and Grady, 1999; Leshin and Vicenzi, 2006). Lazzeri *et al.* (2017) suggested that, if present in siliceous alteration products at/near the martian surface, phases such as melanophlogite (a silica clathrate) could incorporate and store N (and C), potentially preserving records of biogeochemical processing.

During alteration of volcanic rocks on the seafloor, glasses are easily replaced by hydrous phases such as clays and zeolites and, in some cases, appear to show evidence of microbial alteration (see Staudigel *et al.*, 2006, 2008; Fisk and McLoughlin, 2013). Because metastable volcanic glass alters more readily than silicate minerals in the same rocks, the glass contributes more significantly to the overall chemical mass-balance of seafloor alteration (Staudigel and Hart, 1983). Previous work has demonstrated that whole-rock samples of altered oceanic crust on the seafloor can contain up to 18 ppm N with elevated $\delta^{15}\text{N}$ relative to that of unaltered oceanic crust (Busigny *et al.*, 2005; Li *et al.*, 2007). This N enrichment has been interpreted as reflecting interaction of these rocks with low-temperature hydrothermal fluids containing mobilized seawater organic N, thus

stabilizing NH₄⁺-bearing alteration minerals. However, the work on whole-rock samples does not allow identification of the specific sites of this N in such rocks or comparison of any N enrichment with other alteration at fine scales.

Recent measurements by the Mars Science Laboratory (MSL) Curiosity rover have indicated that a substantial proportion of the near-surface regolith consists of X-ray amorphous materials, associated with a variety of crystalline phases including plagioclase feldspar, clinopyroxene, and olivine (Blake *et al.*, 2013). These mineral assemblages are quite consistent with altered basalts, and terrestrial palagonite (a fine-grained intergrowth of various clays, zeolites, and oxides; Stronck and Schmincke, 2001, 2002; Pauly *et al.*, 2011) is commonly X-ray amorphous. The martian basaltic breccia meteorites (NWA 7034 and its pairing group) contain abundant basaltic glass, predominantly of impact origin (Wittmann *et al.*, 2015). Spectroscopic measurements show that reflectance spectra of NWA 7034 match those of large areas of the martian surface, demonstrating the ubiquity of basaltic glass on the surface of Mars (Cannon *et al.*, 2015b). Therefore, it is possible that altered glassy materials (likely a mixture of impact and volcanic glasses) are abundant and widely distributed on Mars, at locations where hydrothermal or other solutions have interacted with glass.

We investigated the possibility that, on Earth, organic N is stored in altered basalts in palagonite, and perhaps also in part in texturally related tubules thought to be of possible microbial origin. As a preliminary study, we examined variably palagonitized glasses from the Troodos ophiolite and Stonyford volcanics (both Mesozoic) for N contents and $\delta^{15}\text{N}$ as an assessment of the potential of these materials as biological tracers. For ODP Site 1256 (offshore of Costa Rica), data for altered glasses were compared with those for whole-rock samples to determine the extent to which the alteration and related N enrichment is controlled by the abundance and N concentrations of the variably altered glasses. We discuss the implications of N enrichment during palagonitization of terrestrial volcanic glass for the use of N as a tracer of past and modern biological activity on Mars and other extraterrestrial bodies.

2. Sampling Localities

We investigated the possible incorporation of N during alteration into volcanic glasses obtained from drilling of the modern seafloor (at ODP Site 1256) and separated from Mesozoic ophiolites exposed on Cypress (Troodos ophiolite) and in California (Stonyford volcanics). Microbial ichnofossils have been described for each of the suites we investigated, and in particular, the possibly microbe-related alteration in the Troodos glasses has seen considerable attention in studies employing various microanalytical imaging and spectroscopic methods (see Furnes *et al.*, 2001; Staudigel *et al.*, 2008; Knowles *et al.*, 2012, 2013; Wacey *et al.*, 2014; Banerjee and Izawa, unpublished data).

2.1. ODP Site 1256 (modern seafloor)

Site 1256 is located on the Cocos Plate in ocean crust formed at the East Pacific Rise (see Santelli *et al.*, 2010). At the time of crust formation (~ 15 Ma), the full spreading rate was $\sim 200\text{--}220$ mm/yr (Wilson, 1996). Underlying

251 m of pelagic sediments, the volcanic crust is dominated by basaltic sheet flows with chilled margins, massive flows (the most predominant one occurring at the sediment/basement interface similar to Hole 1253), subordinate flows of pillow lavas, breccias, and rare dikes (Wilson *et al.*, 2003). Hole 1256D has been subsequently deepened to 1507 m below seafloor through sheeted dikes and into gabbro (Wilson *et al.*, 2006).

2.2. Troodos ophiolite (Mesozoic)

The Cretaceous Troodos ophiolite of Cyprus contains all the components of a complete ophiolite (including an abundance of fresh glass) and has been investigated extensively (*e.g.*, Panayiotou, 1980; Robinson *et al.*, 1983; Malpas *et al.*, 1990). Over half the volcanic rocks are pillow lavas, and the remaining are breccias associated with pillows and sheet flows (Schmincke *et al.*, 1983; Schmincke and Bednarz, 1990). Textural studies have revealed that the altered basaltic glasses here reach to depths of at least 550 m into the volcanic basement (Thorseth *et al.*, 1995; Furnes *et al.*, 1996, 1999; Fisk *et al.*, 1998; Torsvik *et al.*, 1998; Furnes and Staudigel, 1999).

2.3. Stonyford volcanics (Mesozoic)

The Stonyford volcanic complex is a thick accumulation of pillow basalt and diabase of Late Jurassic age in the northern Coast Ranges of California (Brown, 1964; Hopson *et al.*, 1981; Shervais and Kimbrough, 1987; Shervais and Hanan, 1989). Glasses in this area, first reported by Brown (1964), occur within the pillow basalts and appear to be remarkably unaffected by later metamorphic or alteration processes (Shervais and Hanan, 1989). Lava flows in the Stonyford volcanics include both pillow lava and sheet flows, but massive sheet flows seem to be the dominant flow type. The base of the seamount sequence, which lies to the southwest and west, is dominated by massive flows of oceanic tholeiite, with intercalations of pillow lava (Shervais *et al.*, 2005).

3. Analytical Methods

3.1. Methods for the analyses of N concentrations and isotopic compositions (done at Lehigh University)

Glass N concentrations and isotopic compositions were analyzed by using the carrier gas methods described by Bebout *et al.* (2007; also see Li *et al.*, 2007). Nitrogen extracted (in the form of N₂) was purified in an all-metal extraction line, then transferred into a Finnigan MAT 252 mass spectrometer via a Finnigan Gas Bench II and a U-trap interface where small samples of N₂ were entrained in a He stream. For the Mesozoic ophiolites, a binocular microscope was used to separate glass samples into clean (black and glassy) and altered (glass with dull brown encrustations) fractions, which were then crushed. For the ODP Site 1256 samples, glass separates were similarly separated, using a binocular microscope, but no effort was made to separate altered and less altered glass. About 100–500 mg of clean and altered glass samples were loaded into quartz tubes with 1 g of CuO_x reagent and evacuated for 24 h on a vacuum manifold before sealing. Tubes were heated at 1050°C for 180 min in a programmable furnace, and the cooling history

was very carefully regulated to ensure speciation of N as N₂ (see Bebout and Sadofsky, 2004, for description of methods). Variations in the isotopic composition of N in unknown samples are reported using conventional delta notation where the standard is atmospheric N₂.

One issue involving sample treatment with particular relevance to our results is the method by which the samples were preheated, compared with the methods used by Busigny *et al.* (2005). In the study of these latter authors, samples were preheated, prior to extractions, at a temperature of 450°C in an oxidizing environment, whereas in our work on similar samples (see Bebout *et al.*, 2007; Li *et al.*, 2007), a preheating temperature of ~100°C was selected (at high vacuum, not in an oxidizing environment). At the preheating conditions employed by Busigny *et al.* (2005), a significant amount of N could be released, for example, from the clay minerals and the zeolites, both identified in altered oceanic crustal rocks. In this paper, we provide a comparison of results obtained for ODP Site 1256 by having used the two preheating methods. We suggest that studies of N and other volatile components in samples of this type that are returned from Mars should take into careful consideration any preheating regimen involved in the analyses.

3.2. Petrographic/Spectroscopic methods

Optical microscopy (see the example in Fig. 1): Our work identifying and characterizing glasses in our samples was conducted initially in transmitted and reflected light with Nikon LV100 POL petrographic microscopes equipped with Nikon DS-Ri1 12 Mpixel cameras at the University of Western Ontario and Texas Tech University.

Scanning electron microscopy methods (done at the Pheasant Memorial Laboratory [PML], Institute for Planetary Materials, Okayama University): To describe in detail the palagonite and any microbial structures present, double polished thin sections of glass chunks were prepared. The thin sections were coated by ~7 nm of C to reduce electron charging of the sample surface. A field emission scanning electron microscope (JEOL JSM-7001F), equipped with an energy dispersive X-ray spectrometer and Oxford INCA X-Max, was used to investigate texture and elemental distribution. All observations and analyses were conducted under the condition of 15 kV acceleration voltage with 3 nA beam current.

Scanning transmission electron microscopy methods (done at the PML): Transmission electron microscopy was applied to investigate nanometer-scale textures in a Troodos glass sample. Thin films were fabricated from the thin sections by using a focused ion beam technique and the JEOL JIB4500 system equipped with a gallium (Ga) ion gun. Subsequently, both sides of the region of interest were milled by a Ga ion beam focused at 30 kV to produce a 100–150 nm slice. The thin films fabricated in this way were transferred from the thin section to a perforated C film on a Cu grid in a clean bench by using an oil hydraulic manipulator and a borosilicate glass needle with a tip diameter of ~10 μm. Nanotexture imaging was performed by a 200 kV transmission electron microscope (TEM; JEOL JEM-2100F) in STEM mode. To reduce beam damage of the samples, the sample temperature was kept at 77 K [liquid nitrogen temperature] during the experiment with a cryogenic cooling holder. For high-resolution TEM imaging,

FIG. 1. Photomicrographs (in plane-polarized light; same magnification) showing two examples of alteration assemblages in the Stonyford volcanics, including multiple possible environments for the incorporation of N (Banerjee and Izawa, unpublished data). MT (in **A** and **B**): Mineralized tubules (mineralized by fine-grained titanite) within zeolite-dominated alteration zones. Z (in **A** and **B**): Zeolite-dominated alteration, containing Ca-phillipsite, analcime, heulandite, and Ca-stilbite. HT (in **B** only): Hollow tubules (or mostly hollow, some contain small amounts of phyllosilicates and other alteration materials and possibly organic compounds) within unaltered basaltic glass (yellow-brown). Basaltic glass is not expected to be a major carrier of N due to the generally low solubility of N in basaltic liquids. Nitrogen, as NH_4^+ , is likely to be incorporated into the palagonite alteration materials via substitutions such as NH_4^+ for K^+ , particularly in phyllosilicate components. Ammonium substitution for alkali ions may also occur in the zeolitic alteration assemblages along with incorporation of N species as free molecules (e.g., N_2 , NH_3) in the large cage sites of zeolite minerals. There could be a very small contribution from N incorporated in organic compounds, as was suggested for Troodos glasses by Wacey *et al.* (2014).

we employed a high-resolution CCD equipped with an energy-filtered imaging system (GATAN GIF Tridiem 863).

4. Results

4.1. ODP Site 1256

The combination of whole-rock samples and glass separates from Site 1256 analyzed in this study shows little retention of values typically associated with fresh mid-ocean ridge basalt (MORB) glass ($-5 \pm 2\text{‰}$; see Cartigny and Marty, 2013; see Table 1 and Fig. 2). Nitrogen concentrations range from 3 to 17.8 ppm, with one glass sample showing a far higher concentration of 75 ppm. All samples have $\delta^{15}\text{N}_{\text{air}}$ higher than that of fresh MORB ($-5 \pm 2\text{‰}$), with values ranging from -1.7 to $+4.5\text{‰}$. Neither the concentrations nor the isotopic compositions show obvious correlation with depth in the Site 1256 core. The $\delta^{15}\text{N}$ values obtained for these Site 1256 samples are shifted toward values of about $+5$ to $+8\text{‰}$ for the hemipelagic sediment section cored at ODP Site 1039 (Li and Bebout, 2005); however, that site is located just outboard of the Costa Rica trench, and a large part of this hemipelagic section was deposited nearer the trench, at an elevated sedimentation rate, relative to the present Site 1256 location.

4.2. Troodos and Stonyford volcanic glasses

Nitrogen concentrations and $\delta^{15}\text{N}$ values for each sample are presented in Table 1 and Fig. 3. The more palagonitized glasses from the Troodos ophiolite and the Stonyford volcanics typically have higher N concentrations and $\delta^{15}\text{N}$ values than less-altered glass separates (see the lines connecting these data in Fig. 3). Glasses from the Troodos

ophiolite contain 2–13.5 ppm N for cleaner glasses and 4.8–53 ppm for the more altered glasses. The $\delta^{15}\text{N}$ of the Troodos glasses ranges from -7.3 to $+5.5\text{‰}$ for clean glasses and -5.3 to $+7.0\text{‰}$ for more altered glasses. Glasses from the Stonyford volcanics contain 3.5–33 ppm N for

TABLE 1. NITROGEN CONTENTS AND $\delta^{15}\text{N}$, ODP SITE 1256D

Sample number*	N (ppm)	$\delta^{15}\text{N}_{\text{air}}$	Meters bsf
1256D 14R-2 68-71	9.5	-0.5	362
1256D 20R1 27-29	75	-1.7	388
1256D 21R1 109-112	11.2	3.3	398
WR 206-1256D 21R-1 124-130	6.4	0.1	398
1256D 21R-2 20-23	17.1	1.7	400
1256D 400	6.0	-0.5	400
WR 1256D 26R-1 42-50	12.1	1.4	439
1256D 30R-1 29-31	12.0	2.4	461
1256D 51R1 110-113	10.5	2.4	461
1256D 461	7.5	0.4	461
WR 206 1256D 41R-2 26-33	11.1	1.7	526
WR 206-1256D 47R-2 121-126	17.8	4.5	574
1256D 583	14.3	1.7	578
WR 1256D 49-1 68-76	11.0	2.1	583
WR 206-1256D 51R-1 45-51	13.2	0.2	597
1256D 598 1	4.5	0.5	598
1256D 598 2	15.1	0.2	598
1256D 51R-2 68-71	3.0	2.2	599
1256D 51R-2 38-40	17.5	2.3	599
WR 206-1256D 52R-1 8-15	9.1	1.3	601
1256D 62R-1 5-8	3.8	2.8	687

*Volcanic glass separates unless indicated as being "WR" (whole-rock samples).

FIG. 2. Plot of N concentration (above) and $\delta^{15}\text{N}$ (below) for ODP Site 1256D glasses and whole-rock samples, versus depth in the drilled oceanic crustal section (see Table 1). Also included are whole-rock data for the same core from Busigny *et al.* (2005; red-filled triangles). Note the lower N concentrations and higher $\delta^{15}\text{N}$ values in the data set from this other study (see the discussion of the analytical methods employed in this study vs. those employed in the other study).

clean glasses and 13–45 ppm for altered glasses. The $\delta^{15}\text{N}$ of the Stonyford glasses ranges from -7.2 to -3.9 ‰ for clean glasses and -6.3 to -2.6 ‰ for altered glasses. Some Stonyford volcanics glasses (with and without observable alteration; see Fig. 3) are enriched in N relative to fresh MORB glass but have mantle-like $\delta^{15}\text{N}$ of -8 to -4 ‰.

4.3. Imaging and geochemical observations

Figures 4–7 present images obtained by scanning electron microscope (SEM) and scanning transmission electron mi-

FIG. 3. Nitrogen concentrations and isotopic compositions of volcanic glasses showing more alteration (in square boxes) and less alteration (no boxes, connected by lines to more altered glass from the same sample), as judged microscopically from varying amounts of palagonite developed on edges of grains (see Table 2). Samples are from Cyprus (CYP) and the Stonyford volcanics, California (SFV). HYAL = glass from hyaloclastite from Cyprus. Note that, in most cases, the more altered glass has a higher N concentration and higher $\delta^{15}\text{N}$ value (gray squares indicate lower $\delta^{15}\text{N}$ values). Note also that the SFV glasses retain near “mantle values” of $\delta^{15}\text{N}$ (-5 ± 2 ‰; gray-shaded box in lower left of figure; see Cartigny and Marty, 2013) despite N enrichment, possibly reflecting incorporation, during palagonitization, of N degassing from the crystallizing and cooling volcanic rocks. The inset photomicrograph is of putative microbial ichnofossils near a palagonitized fracture (the latter oriented from upper left to lower right) in glass from the Stonyford volcanics (horizontal dimension is 200 μm ; example of putative microbial feature is indicated by arrow).

croscope (STEM), demonstrating textures and chemical alteration in, and adjacent to, palagonitized fractures in the glasses from the two Mesozoic ophiolites. The back-scattered electron image and element maps in Fig. 4 demonstrate alteration along two intersecting palagonitized cracks in volcanic glass. Areas directly adjacent to these cracks show depletions in a number of elements but with enrichments in the same elements directly along the cracks (most obviously K, Mg, Si, Ca, Ti, Al, and Fe). For Al, Si, Ti, and Ca, these enrichments appear to correspond to the presence of titanite along the more vertically oriented crack. Titanite has been observed along microtubules, as an example demonstrated by the coenrichments in Al, Si, Ti, and Ca in the image of a cross section of one microtubule in Fig. 6 (*cf.* Izawa *et al.*, 2010). Mineralization by titanite has been argued as a preservation mechanism for ichnofossils in basaltic glass (*e.g.*, Furnes *et al.*, 2004; Banerjee *et al.*, 2006; Staudigel *et al.*, 2008). Elevated concentrations of K (Fig. 5) may indicate the presence of illite or other potassic

FIG. 4. SEM imaging of mineralized cracks in glasses from the Stonyford volcanics. (Top panel) SEM image, showing two intersecting cracks with obvious alteration. (Bottom panels) Element maps for the same region, showing element distributions in and adjacent to the cracks. The Ca-Ti-Al-Si-rich zones likely correspond to concentrations of titanite (CaTiSiO_5). Potassium is enriched at the location of the initial fracture along which the alteration occurred. For all element maps, higher concentrations are represented by warmer colors, low concentrations are represented by cooler colors, and colors are ordered as in the electromagnetic spectrum.

phyllosilicate minerals, which may be a repository of N as NH_4^+ . Lattice fringes (Fig. 7) showing basal spacings of ~ 1.0 nm (10 Å) and ~ 1.3 nm (13 Å) are consistent with an intergrowth of illite and smectite, respectively (e.g., Vali and Köster, 1986; Murakami *et al.*, 2005).

5. Discussion

5.1. Residency of N and significance of the N isotope compositions of the glasses

The N in these palagonitized glasses most likely resides in clays and zeolites as NH_4^+ and possibly in the zeolites also as molecular N_2 (see Teunissen *et al.*, 1993; discussion by Kolesov and Geiger, 2003). Among the possible clay minerals, illite (a K^+ -rich phase) is known to incorporate large amounts of N, as NH_4^+ (e.g., Bobos and Eberl, 2013). Mixed-layer illite-smectite is known to contain significant amounts of NH_4^+ , but likely largely in illitic domains (Drits *et al.*, 1997). The degree to which a pure smectite will incorporate NH_4^+ is not known, but such incorporation could occur via a charge balance during substitution of Si^{+4} by M^{+3} (Chourabi and Fripiat, 1981). This would be of great interest in considering the possible incorporation of NH_4^+ by the abundant nontronite (Fe-rich smectite) observed on the martian surface (see Ehlmann and Edwards, 2014). Ammonium is also likely to be incorporated into zeolite in palagonite, although the dependence of this incorporation on the exact zeolite present, and the degree to which this NH_4^+ can be stored for longer time periods, is not known. For the Stonyford volcanics glasses (see Fig. 1), zeolite-dominated alteration involves Ca-phillipsite $[(\text{Ca}, \text{Na}_2, \text{K}_2)_3\text{Al}_6\text{Si}_{10}\text{O}_{32} \cdot 12\text{H}_2\text{O}]$ as the dominant zeolite species, with other phases including analcime $[\text{NaAlSi}_2\text{O}_6 \cdot \text{H}_2\text{O}]$, heulandite $[(\text{Ca}, \text{Na})_{2-3}\text{Al}_3(\text{Al}, \text{Si})_2\text{Si}_{13}\text{O}_{36} \cdot 12\text{H}_2\text{O}]$, and Ca-stilbite $[\text{NaCa}_4(\text{Si}_{27}\text{Al}_9)\text{O}_{72} \cdot 28(\text{H}_2\text{O})]$ (Banerjee and Izawa, unpublished data). The residency of NH_4^+ in other amorphous (gelatinous) and crystalline components during the textural and mineralogical evolution of palagonite (Stronck and Schmincke, 2001) is also unknown.

All the altered glass samples analyzed in this study (Figs. 2 and 3) have N concentrations higher than those of “fresh” MORB (the latter typically containing <2 ppm N; see Cartigny and Marty, 2013), reflecting significant N enrichment in these samples relative to their unaltered counterparts. For the Stonyford volcanics glasses, the observed shifts from MORB-like N concentrations, with and without positive shifts in $\delta^{15}\text{N}$ from fresh MORB values (see Fig. 3), could indicate that early-formed palagonite incorporated degassed mantle-derived N, with later-formed palagonite incorporating sedimentary/organic N introduced by pore fluids. Circulation of hydrothermal fluids induced by the magmatic intrusion could have leached NH_4^+ from coexisting and overlying sediments. This NH_4^+ could then have been fixed into secondary clay minerals and bound to the glasses. Studies of whole-rock N enrichment and $\delta^{15}\text{N}$ in altered basalts from the modern seafloor (Busigny *et al.*, 2005; Li *et al.*, 2007) have similarly demonstrated additions of N with $\delta^{15}\text{N}$ elevated relative to the mantle-like values of fresh basalts (also see the whole-rock data in Fig. 2).

The apparent incorporation of sedimentary/organic N signatures (shifts toward positive $\delta^{15}\text{N}$) in the highly reactive (metastable) glasses indicates that they can provide one record of the N biogeochemical cycling at the time of the alteration. The $\delta^{15}\text{N}$ of seafloor sediment on modern Earth is mostly in the range of $+2$ to $+12\text{‰}$ (see the compilations in Sadofsky and Bebout, 2004; Cartigny and Marty, 2013; Tesdal *et al.*, 2013). It is uncertain whether microbial N is directly measured in analyses such as ours, and rather more likely that any microbial N is now incorporated into clays and highly diluted by N added in the pore fluids. Wacey *et al.* (2014) demonstrated that some microtubules in

FIG. 5. STEM imaging of mineralized cracks in Troodos glasses. (a) STEM dark-field image, showing a crack in the glass with a nearby and seemingly genetically related phyllosilicate aggregate (interpretive sketch **b**). (c–f) Element maps for Mg, Ca, Fe, and K in the same region, showing element distributions in and adjacent to the crack and in the phyllosilicate aggregate. Note that, although the altered area is depleted in K, the edge of the alteration front shows enrichment in that element.

Troodos glasses are lined with C and minor N, raising the possibility of some relict microbial N.

5.2. The possible role of microbial processes

Multiple complementary lines of evidence demonstrate that microbial life rapidly colonizes subaqueously emplaced terrestrial glassy basaltic rocks (Torsvik *et al.*, 1998; Banerjee and Muehlenbachs, 2003; Furnes *et al.*, 2004; Banerjee *et al.*, 2006; Benzerara *et al.*, 2007; McLoughlin *et al.*, 2009; Preston *et al.*, 2011; Fisk and McLoughlin, 2013). Microbial ichnofossils have been described for each of the suites we investigated, and in particular, the microbe-related alteration in the Troodos glasses has seen considerable attention in studies employing various microanalytical imaging and spectroscopic methods (see Furnes *et al.*, 2001; Staudigel *et al.*, 2008; Knowles *et al.*, 2012, 2013; Wacey *et al.*, 2014). However, as noted earlier, any role of microbes in producing the N enrichments and elevated $\delta^{15}\text{N}$ values reported in this paper remains uncertain.

Evidence for the microbial alteration of oceanic crust has been reported for the modern seafloor, ophiolites, and Archean greenstone belts extending to ~ 3.5 Ga (see Banerjee *et al.*, 2006; Staudigel *et al.*, 2008). Surfaces of cavities etched by microbes often contain traces of microbial DNA or organic C residues and show uneven distributions on X-ray maps of biologically active elements such as N, K, P,

S, and transition metals (*e.g.*, Banerjee *et al.*, 2010). 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 (Torsvik *et al.*, 1998; Banerjee and Muehlenbachs, 2003; Furnes *et al.*, 2004; Banerjee *et al.*, 2006; Benzerara *et al.*, 2007). The geological impact of glass bioalteration could be substantial because it has been found everywhere in ocean drill holes, and it can play an important role in the glass alteration in any age crust, typically with optimum growth conditions between 15°C and 80°C (Furnes and Staudigel, 1999; Walton and Schiffman, 2003). In addition, bioalteration was found in nearly all well-preserved ophiolites and greenstone belts, suggesting that this process is pervasive, affecting close to 60% of Earth's surface area, to a significant depth, throughout geological time (Staudigel *et al.*, 2008). Nitrogen incorporated into seafloor basalts by this process could contribute to the N subduction budget (see Li *et al.*, 2007).

5.3. Implications for Earth ocean-to-mantle N cycling

The geochemistry of N discharged by magmatism at mid-ocean ridges and in volcanic arcs has been investigated in some detail, including work focused on several individual convergent margins that greatly improves our understanding

FIG. 6. SEM imaging of a cross section of an individual microtubule in a glass from the Stonyford volcanics. (Top panel) SEM back-scattered electron image, showing the cross section of the microtubule. (Bottom panels) Element maps for the same region, showing element distributions in and adjacent to the microtubule.

of N return in arcs (*e.g.*, Hilton *et al.*, 2002; Li *et al.*, 2007). Altered oceanic crust, including altered glasses, subducting into modern trenches could play a key role in the crust-mantle cycling of N (Li and Bebout, 2005; Li *et al.*, 2007). Li and Bebout (2005) highlighted that, because the volume of oceanic crust is far greater than that of the overlying sediments, the N subduction budget in oceanic crust could for some margins be comparable to that in sediments (also see Bebout, 1995; Hilton *et al.*, 2002; Halama *et al.*, 2010). Anderson *et al.* (2018) suggested the possibility of similar incorporation of biologically processed N in 2.7 Ga metabasaltic rocks of the Abitibi greenstone belt.

FIG. 7. TEM images of a phyllosilicate-rich region in a Troodos glass (see Fig. 5). (A) STEM dark-field image of intergrowth of clay minerals, probably smectite and illite. (B) HRTEM image illustrating d-spacing indicative of the presence of smectite and illite (Murakami *et al.*, 2005), each phase (but particularly illite) capable of incorporating N as NH_4^+ (black scale bar = 10 nm; horizontal width of image is 95 nm).

5.4. Implications for astrobiology

Recently published spectral studies have proposed the abundance of palagonite (hydrothermally altered basaltic glass) on the martian surface (see the review by Ehlmann and Edwards, 2014). Recent X-ray diffraction analysis *in situ* by MSL CheMin has shown large quantities of an X-ray amorphous material that could contain a significant proportion of palagonite-like material, that is, aqueously altered mafic composition glass. This palagonite could similarly have incorporated N during its alteration, potentially providing a record of the N biogeochemical pathways of N on Mars at that time. This record would be complicated by the unknown $\delta^{15}\text{N}$ of the martian atmosphere at the time of incorporation, but it could conceivably provide a record of the atmospheric evolution. Phyllosilicate- and zeolite-rich alteration could have developed in/near impact craters on ancient Mars, providing a setting in which microbial life could have at least temporarily flourished. It is unknown whether the records of

$\delta^{15}\text{N}$ shift presented in this paper directly reflect microbial biomass or deposits left behind by microbial activity—the records could instead have resulted from water-glass interaction in permeability produced by cracking and potentially also microbial burrowing.

Records of N enrichment in palagonitized martian basalts, with or without occurrences of microbial tubules, could reflect ancient biological processes, as these basalts were likely hydrated early in the planet's history when liquid H_2O had access to rapidly cooling basaltic lavas (Wyatt and McSween, 2006). Ultimately, for any altered basaltic rocks returned from Mars, geochronology will be required to determine the timing of this alteration. Spectral studies of the modern martian surface have demonstrated an abundance of altered basalts containing clay minerals and zeolites, both with the potential to contain N, in clays as NH_4^+ and in zeolites possibly as both NH_4^+ and N_2 . Altered basaltic rocks, along with any ultramafic rocks (see Li *et al.*, 2016), should be a target for future sample return as, with or without microbial components, the alteration can inform us regarding the chemical environment of this hydrous alteration at/near the ancient martian surface. Investigations of martian meteorites using the analytical approaches taken here could provide important new insights into the martian N cycle and, by studying martian meteorites of a variety of ages, the time-evolution of this cycling.

Of course, on Earth, biological activity (at the least microbial) is expected in essentially any surface/near-surface setting, and the N isotope compositions of the biological and mantle reservoirs are well characterized. This allows relatively easy interpretation of data sets such as those presented in Figs. 2 and 3. For study of altered basaltic glasses returned from Mars, it will be necessary to take a multiple-tracer approach examining major and trace element and stable isotope records (C, N, H, O), including N and C, the latter which together have particular potential to serve as biosignatures. Such work will also test for evidence of the redistribution and, in some cases, isotope compositions of certain trace elements indicative of biological processing (P, transition metals such as Fe, Mo, V, Cr, Mn, Co, Ni, Cu, Zn, and W; Ehrlich, 1997; Glass *et al.*, 2009; Banerjee *et al.*, 2010; Godfrey and Glass, 2011). A multiple-proxy approach

will be preferable to any attempt to identify and associate an individual chemical or isotope shift to biological activity (see van Zuilen, 2007; Staudigel *et al.*, 2008; Summons *et al.*, 2011; Westall *et al.*, 2011; McLoughlin and Grosch, 2015). Work prior to this sample return should endeavor to identify the combinations of stable isotope compositions (*e.g.*, N, C, H, O, S, but also Fe, Mo, Cr, etc.), element concentrations (*e.g.*, transition metals, P; see Banerjee *et al.*, 2010), organic chemistry, and morphology best able to provide a demonstration of any extant or past biological processes. The data in Tables 1 and 2 demonstrate that one important by-product in any future analyses of variably altered volcanic glass returned from Mars will be the evidence regarding magmatic sources and processes obtainable through analyses of the unaltered volcanic glasses (*e.g.*, C, N, H, and O isotope compositions of magma sources). The lines in Figs. 2 and 3 demonstrate the trajectories in N concentration and $\delta^{15}\text{N}$ taken with increasing degrees of palagonitization, pointing to the unaltered compositions corresponding to known Earth upper-mantle values.

6. Conclusions

The results presented here constitute an exploratory study of the incorporation of N, largely through low-temperature hydrothermal alteration, into volcanic glass from the modern seafloor (ODP Site 1256) and Mesozoic volcanic glasses from Cyprus and the Franciscan complex. All samples investigated in this study contain measurable quantities of N, and palagonitized glasses from both sites typically have higher N concentrations (up to 53 ppm) and $\delta^{15}\text{N}$ values than those of less-altered glass separates from the same samples. All altered glasses have N concentrations higher than those of fresh MORB (typically <2 ppm N; Cartigny and Marty, 2013), reflecting significant N enrichment in these glass samples relative to the concentrations that can be attributed to magmatic processes. The observed shifts in N concentrations and $\delta^{15}\text{N}$ can be attributed to incorporation of sedimentary/organic N introduced by pore fluids. Circulation of hydrothermal fluids, perhaps induced by heat from the nearby magmatism, could have leached NH_4^+ from co-existing and overlying sediments then fixed to glasses. This alteration could continue during the longer-term transit of oceanic crust across ocean basins and toward subduction zones at which it contributes to the seafloor N inventory subducting into the mantle. Although the samples investigated in this study in many cases contain textural evidence for microbial alteration, and considerable mineralization occurs in these microtubules, direct association of the N enrichments with this microbial alteration awaits a micro-analytical method for analyzing the isotopic compositions of the N at the scale investigated in recent microanalytical imaging and spectroscopic studies (*e.g.*, Wacey *et al.*, 2014).

These findings should be taken into consideration in planning strategies for the search for (modern and ancient) life on Mars and other extraterrestrial bodies. The enhanced chemical reactivity of volcanic glass makes it a potentially useful receptacle for biologically (or nonbiologically) fixed N that could yield information regarding the biogeochemical pathways at the time of incorporation. Future Mars sample return missions should prioritize return of palagonitized basaltic glasses, in intact basaltic exposures or blocks or in

TABLE 2. ISOTOPIC DATA FOR VOLCANIC GLASSES
CYPRUS AND STONYFORD VOLCANICS

Sample	Clean*		Altered*	
	$\delta^{15}\text{N}_{\text{air}}$	N (ppm)	$\delta^{15}\text{N}_{\text{air}}$	N (ppm)
CYP-01	−1.8	2.4	+1.8	5.8
HYAL-02	−7.3	2	−5.3	4.8
CYP-03	4.3	11.6	+6.1	53
CYP-04	5.5	13.5	+7	49
CYP-05	4.5	9	+1.4	9.2
CYP-009	−3.8	9.7	−1.5	8.4
CYP-011	0.4	5.7	−2.5	6.9
SFV-G2	−7.2	22	−2.6	30
SFV-G3	−5.4	33	−3	45
SFV-G4	−6.7	18.8	−6.3	28
SFV-G5	−3.9	18	−4.3	13
SFV-G8	−4.7	3.5	−5.7	16

*As deduced by examination under a microscope, based on the abundance of brownish, palagonitized glass.

immature sandstones and conglomerates (see Cannon *et al.*, 2015a), with the hope that these glasses retain information regarding modern or ancient N biogeochemical cycling.

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Address correspondence to:

G.E. Bebout

Department of Earth and Environmental Sciences

Lehigh University

1 W. Packer Avenue

Bethlehem, PA 18015

E-mail: geb0@lehigh.edu

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Abbreviations Used

MORB = mid-ocean ridge basalt
 MSL = Mars Science Laboratory
 PML = Pheasant Memorial Laboratory
 SEM = scanning electron microscope
 STEM = scanning transmission electron microscope
 TEM = transmission electron microscope