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

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Abstract

Observed enrichments of N (and the δ^{15}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 δ^{15}N_{air} values of up to +4.5‰. Variably altered glasses from Mesozoic ophiolites (Troodos, Cyprus; Stonyford volcanics, USA) contain 2–53 ppm N with δ^{15}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 δ^{15}N considerably higher than that of their unaltered glass equivalents (for MORB, −5±2‰). Circulation of hydrothermal fluids, in part induced by nearby spreading-center magmatism, could have leached NH₄⁺ from sediments then fixed this NH₄⁺ 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 δ^{15}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 N₂, including NH₄⁺ (ammonium), NH₃ (ammonia), and NO₃⁻ (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 N₂ 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 NH₄⁺ bound in aluminosilicate minerals. Several groups have been studying N cycling in the...
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 Ehmann 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; Ehmann 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⁺, NO₃⁻, 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 Nakhla (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 melamaphlogite (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 δ¹⁵N 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; Stroncick 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 δ¹⁵N 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 Cyprus (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 ~200–220 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/base- ment 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 pil- lows 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 Là et al., 2007). Nitrogen extracted (in the form of \( \text{N}_2 \)) 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 \( \text{N}_2 \) 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 \( \text{CuO} \), reagent and evacuated for 24 h on a vacuum manifold before sealing. Tubes were heated at \( 1050^\circ \text{C} \) for 180 min in a programmable furnace, and the cooling history was very carefully regulated to ensure speciation of \( \text{N} \) as \( \text{N}_2 \) (see Bebout and Sadofsky, 2004, for description of methods). Variations in the isotopic composition of \( \text{N} \) in unknown samples are reported using conventional delta notation where the standard is atmospheric \( \text{N}_2 \).

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 \( 450^\circ \text{C} \) in an oxidizing environment, whereas in our work on similar samples (see Bebout et al., 2007; Li et al., 2007), a preheating temperature of \( \approx 100^\circ \text{C} \) was selected (at high vacuum, not in an oxidizing environment). At the preheating conditions employed by Busigny et al. (2005), a significant amount of \( \text{N} \) 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 \( \text{N} \) 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 \( \approx 7 \) 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 \( \approx 10 \mu \text{m} \). 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,
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 to −2 ppm; 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 $d_{15}^{\text{N}}$air higher than that of fresh MORB (−5 to −2), with values ranging from −1.7 to +4.5. Neither the concentrations nor the isotopic compositions show obvious correlation with depth in the Site 1256 core. The $d_{15}^{\text{N}}$ values obtained for these Site 1256 samples are shifted toward values of about +5 to +8 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 $d_{15}^{\text{N}}$ 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 $d_{15}^{\text{N}}$ 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 $d_{15}^{\text{N}}$ of the Troodos glasses ranges from −7.3 to +5.5 for clean glasses and −5.3 to +7.0 for more altered glasses. Glasses from the Stonyford volcanics contain 3.5–33 ppm N for

Table 1. Nitrogen Contents and $d_{15}^{\text{N}}$, ODP Site 1256D

| Sample number* | N (ppm) | $d_{15}^{\text{N}}$air | Meters bsf |
|----------------|---------|------------------------|------------|
| 1256D 14R-2 68-71 | 9.5 | −0.5 | 362 |
| 1256D 20R1 27-29 | 75 | −1.7 | 388 |
| 1256D 21R 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).
clean glasses and 13–45 ppm for altered glasses. The $\delta^{15}$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 $\delta^{15}$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 microscope (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
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 Ehlimann 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-philippsite [(Ca$_4$Na$_2$K$_2$)$_2$Al$_4$Si$_{12}$O$_{32}$·12H$_2$O] as the dominant zeolite species, with other phases including analcime [NaAlSi$_2$O$_6$·H$_2$O], heulandite [(Ca$_4$Na$_2$)$_2$Al$_2$(Al,Si)$_2$Si$_3$O$_{36}$·12H$_2$O], and Ca-stilbite [NaCa$_4$(Si$_{27}$Al$_9$)O$_{72}$·28(H$_2$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 (Stroncik 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 $\delta^{15}$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 $\delta^{15}$N in altered basalts from the modern seafloor (Busigny et al., 2005; Li et al., 2007) have similarly demonstrated additions of N with $\delta^{15}$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 $\delta^{15}$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 $\delta^{15}$N of seafloor sediment on modern Earth is mostly in the range of +2 to +12‰ (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...
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 $\delta^{15}$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 $\sim$3.5 Ga (see Banerjee et al., 2006; Staudigel et al., 2008). Surfaces of cavities etched by microbes often contain traces of microbial DNA or organic C residues and show uneven distributions on X-ray maps of biologically active elements such as N, K, P, S, and transition metals (e.g., Banerjee et al., 2010). Altered glassy basaltic rocks have the potential to retain a variety of signatures of past biological activity including microbial alteration textures (ichnofossils), element distributions, organic compounds, and isotopic compositions (Torsvik et al., 1998; Banerjee and Muehlenbachs, 2003; Furnes et al., 2004; Banerjee et al., 2006; Benzerara et al., 2007). The geological impact of glass bioalteration could be substantial because it has been found everywhere in ocean drill holes, and it can play an important role in the glass alteration in any age crust, typically with optimum growth conditions between 15$^\circ$C and 80$^\circ$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.
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.

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 $\delta^{15}$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
\(\delta^{15}N\) 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\(_2\)O 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; Staudeigel et al., 2008; Summons et al., 2011; Westall et al., 2011; McLoughlin and Groesch, 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 \(\delta^{15}N\) taken with increasing degrees of palagonitization, pointing to the unaltered compositions corresponding to known Earth upper-mantle values.

### Table 2. Isotopic Data for Volcanic Glasses Cyprus and Stonyford Volcanics

| Sample  | Clean* \(\delta^{15}N_{air}\) (N ppm) | Altered* \(\delta^{15}N_{air}\) (N ppm) |
|---------|-------------------------------------|-------------------------------------|
| CYP-01  | -1.8 2.4                           | +1.8 5.8                           |
| HYAL-02 | -7.3 2.2                           | -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.

### 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 \(\delta^{15}N\) 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 \(\delta^{15}N\) 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 microanalytical 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
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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References

Anderson, L.D., Bebout, G.E., Izawa, M.R.M., Bridge, N.J., and Banerjee, N.R. (2018) Chemical alteration and preservation of sedimentary/organic nitrogen isotope signatures in a 2.7 Ga seafloor volcanic sequence. International Journal of Astrobiology, in press.

Aoudjehane, H.C., Avice, G., Barrat, J.A., Boudouma, O., Chen, G., Duke, M.J., Franchi, I.A., Gattacceca, J., Grady, M.M., Greenwood, R.C., Herd, C.D., Hewins, R., Jambon, A., Marty, B., Rochette, P., Smith, C.L., Sautter, V., Verchovsky, A., Weber, P., and Zanda, B. (2012) Tissint martian meteorite: a fresh look at the interior, surface, and atmosphere of Mars. Science 338:785–788.

Banerjee, N.R. and Muehlenbachs, K. (2003) Tuff life: bioliteration in volcaniclastic rocks from the Ontong Java Plateau. Geochim Geophys Geosyst 4:1037–1058.

Banerjee, N.R., Furnes, H., Muehlenbachs, K., Staudigel, H., and de Wit, M. (2006) Preservation of ~3.4–3.5 Ga microbially biomarkers in pillow lavas and hyaloclastites from the Barberton greenstone belt, South Africa. Earth Planet Lett 241:707–722.

Bebout, G.E., Izawa, M.R.M., Sapers, H.M., and Whitehouse, M.J. (2010) Geochemical biosignatures preserved in microbially altered basaltic glass. Surf Interface Anal 43:452–457.

Basu, A., Schmitt, J., and Crosesey, L.J. (1999) An argument for zeolites in Mars rocks and an Earth analog [abstract 1041]. In 29th Lunar and Planetary Science Conference, Lunar and Planetary Institute, Houston.

Bebout, G.E. (1995) The impact of subduction-zone metamorphism on mantle-ocean chemical cycling. Chem Geol 126: 191–218.

Bebout, G.E. and Sadofsky, S.J. (2004) δ15N analyses of ammonium-rich silicate minerals by sealed-tube extractions and dual inlet, viscous-flow mass spectrometry. In Handbook of Stable Isotope Techniques, edited by P.A. de Groot, Elsevier, Amsterdam, pp 348–360.

Bebout, G.E., Idleman, B.D., Li, L., and Hilkert, A. (2007) Isotope-ratio-monitoring gas chromatography methods for high-precision isotopic analysis of nanomole quantities of silicate nitrogen. Chem Geol 240:1–10.

Bebout, G.E., Fogel, M.L., and Cartigny, P. (2013) Nitrogen: highly volatile yet surprisingly compatible. Elements 9:333–338.

Bebout, G.E., Lazzeri, K.E., and Geiger, C.A. (2015) Pathways for nitrogen cycling in Earth’s crust and upper mantle: a review and new results for microporous beryl and cordierite. Am Mineral 101:7–24.

Benzerara, K., Menguy, M., Banerjee, N.R., Tyliszczak, T., Guyot, F., and Brown, G.E., Jr. (2007) Alteration of submarine basaltic glass from the Ontong Java Plateau: a STXM and TEM study. Earth Planet Sci Lett 260:187–200.

Bish, D.L., Carey, J.W., Vaniman, D.T., and Chipera, S.J. (2003) Stability of hydrous minerals on the martian surface. Icarus 164:96–103.

Blake, D.F., Morris, R.V., Kocurek, G., Morrison, S.M., Downs, R.T., Bish, D., Ming, D.W., Edgett, K.S., Rubin, D., Goetz, W., Madsen, M.B., Sullivan, R., Gellert, R., Campbell, I., Treiman, A.H., McLennan, S.M., Yen, A.S., Grotzinger, J., Vaniman, D.T., Chipera, S.J., Achilles, C.N., Rampe, E.B., Sumner, D., Meslin, P.Y., Maurice, S., Forni, O., Gasnault, O., Fisk, M., Schmidt, M., Mahaffy, P., Leslin, I.A., Glavin, D., Steele, A., Freissinet, C., Navarro-Gonzalez, R., Yingst, R.A., Kah, L.C., Bridges, N., Lewis, K.W., Bristow, T.F., Farmer, J.D., Crisp, J.A., Stolper, E.M., Des Marais, D.J., and Sarrazin, P. (2013) Curiosity at Gale Crater, Mars: characterization and evolution of the Rocknest sand shadow. Science 341, doi:10.1126/science.1239505.

Bobos, I. and Eberl, D.B. (2013) Thickness distributions and evolution of growth mechanisms of NH₄-illite from the fossil hydrothermal system of Harghite Băi, Eastern Carpathians, Romania. Clays Clay Mineral 61:375–391.

Brides, J.C. and Grady, M.M. (1999) A halite-siderite-anhydrite-chlorapatite assemblage in Nakhla: mineralogical evidence for evaporites on Mars. Meteorit Planet Sci 34:407–415.

Brown, R.D. (1964) Geologic Map of the Stonyford Quadrangle, Glenn, Colusa, and Lake Counties, California, Miscellaneous Field Studies Map MF-279, scale 1:48 000, U.S. Geological Survey, Reston, VA.

Busigny, V. and Bebout, G.E. (2013) Mineralogy, residency, and isotopic behavior of nitrogen. Elements 9:353–358.

Busigny, V., Laverne, C., and Bonifacie, M. (2005) Nitrogen content and isotopic composition of oceanic crust at a superfast spreading ridge: a profile in altered basalts from ODP Site 1256D, Leg 206. Geochim Geophys Geosys 6, doi:10.1029/2005GC001020.

Cannon, K.M., Mustard, J.F., and Salvatore, M.R. (2015a) Alteration of immature sedimentary rocks on Earth and Mars: recording aqueous and surface-atmosphere processes. Earth Planet Sci Lett 417:78–86.

Cannon, K.M., Mustard, J.F., and Agee, C.B. (2015b) Evidence for a widespread basaltic breccia component in the martian low-albedo regions from the reflectance spectrum of North-west Africa 7034. Icarus 252:150–153.

Capone, D.G., Popa, R., Flood, B., and Nealson, K.H. (2006) Vibrational spectra of ammonium in smectites. Clays Clay Minerals 54:260–268.

Ehlmann, B.L. and Edwards, C.S. (2014) Mineralogy of the martian surface. Annu Rev Earth Planet Sci 42:291–315.
McLoughlin, N., Furnes, H., Banerjee, N.R., Muehlenbachs, K., and Staudigel, H. (2009) Ichnotaxonomy of microbial trace fossils in volcanic glass. *J Geol Soc London* 166:159–169.

Murakami, T., Inoue, A., Lanson, B., Meunier, A., and Beaufort, D. (2005) Illite-smectite mixed-layer minerals in the hydrothermal alteration of volcanic rocks: II. One-dimensional HRTEM structure images and formation mechanisms. *Clays Clay Miner* 53:440–451.

Newson, H. (2005) Clays in the history of Mars. *Nature* 438:570–571.

Osinski, G.R., Tornabene, L.L., Banerjee, N.R., Cockell, C.S., Flemming, R., Izawa, M.R.M., McCutcheon, J., Parnell, J., Preston, L.J., Pickersgill, A.E., Poncefract, A., Sapers, H.M., and Southam, G. (2013) Impact-generated hydrothermal systems on Earth and Mars. *Icarus* 224:347–363.

Panayiotou, A., editor. (1980) *Ophiolites: Oceanic Crustal Analogues*, Pergamon Press.

Preston, L.J., Izawa, M.R.M., and Banerjee, N.R. (2011) Infrared spectroscopic characterization of organic matter associated with microbial bioalteration textures in basaltic glass. *Environ Microbiol Rep* 5:648–659.

Panayiotou, A., editor. (1980) *Ophiolites: Proceedings of the International Ophiolite Symposium, Cyprus* 1979, Cyprus Geological Survey Department, Nicosia, Cyprus.

Pauly, B.D., Schiffman, P., Zierenberg, R.A., and Clague, D.A. (2011) Environmental and chemical controls on palagonitization. *Geochem Geophys Geosyst* 12, doi:10.1029/2011GC003639.

Poulet, F., Bibring, J.P., Mustard, J.F., Gendrin, A., Mangold, N., Langevin, Y., Arvidson, R.E., Gondet, B., Gomez, C., Berthé, M., Erard, S., Forqueron, O., Maunaud, N., Pouille, G., Soufflot, A., Combis, M., Drossart, P., Encrenaz, T., Fouchez, T., Melchiorri, R., Bellucci, G., Altieri, F., Formisano, V., Fonti, S., Capaccioni, F., Cerroni, P., Coradini, A., Korabl, O., Kottsov, V., Ignatiev, N., Titov, D., Zasova, L., Pinet, P., Schmitt, B., Sotin, C., Hauber, E., Hoffmann, H., Jaumann, R., Keller, U., Forget, F.; Omega Team. (2005) Phyllosilicates on Mars and implications for early Mars climate. *Nature* 438:623–627.

Preston, L.J., Izawa, M.R.M., and Banerjee, N.R. (2011) Infrared spectroscopic characterization of organic matter associated with microbial bioalteration textures in basaltic glass. *Astrobiology* 11:585–599.

Robinson, P.T., Melson, W.G., O’Hearn, T., and Schmincke, H. (1983) Volcanic glass compositions of the Troodos ophiolite, Cyprus. *Geology* 11:400–404.

Ruff, S.W. (2004) Spectral evidence for zeolite in the dust on Mars. *Icarus* 168:131–143.

Sadofsky, S.J. and Bebout, G.E. (2004) Nitrogen geochemistry of subducting sediments: new results from the Izu-Bonin-Mariana margin and insights regarding global N subduction. *Geochem Geophys Geosys* 5, doi:10.1029/2003GC000543.

Santelli, C.M., Banerjee, N., Bach, W., and Edwards, K.J. (2010) Tapping the subsurface ocean crust biosphere: low biomass and drilling-related contamination calls for improved quality controls. *Geomicrobiol J* 27:158–169.

Schmincke, H.-U. and Bednarz, U. (1990) Pillow, sheet flows and breccia flow volcanoes and volcano-tectonic hydrothermal cycles in the extrusive series of the northeastern Troodos ophiolite, Cyprus. In *Ophiolites: Oceanic Crustal Analogues*, edited by J. Malpas, E.M. Moores, A. Panayiotou, and C. Xenophontos, Cyprus Geological Survey Department, Nicosia, Cyprus, pp 207–216.

Schmincke, H.-U., Rautenschlein, M., Robinson, P.T., and Mehegan, J.M. (1983) Troodos extrusive series of Cyprus: a comparison with oceanic crust. *Geology* 11:405–409.

Shervais, J.W. and Hanan, B.B. (1989) Jurassic volcanic glass from the Stonyford volcanic complex, Franciscan assemblage, northern California Coast Ranges. *Geology* 17:510–514.

Shervais, J.W. and Kimbrough, D.L. (1987) Alkaline and transitional subalkaline metabasalts in the Franciscan Complex melange, California. In *Mantle Metasomatism and Alkaline Magmatism*, Special Paper 215, edited by E.M. Morris and J.D. Pasteris, Geological Society of America, Boulder, CO, pp 165–182.

Shervais, J.W., Murchev, B.L., Kimbrough, D.L., Renne, P.R., and Hanan, B. (2005) Radios isotopic and biostatigraphic age relations in the Coast Range ophiolite, northern California: implications for the tectonic evolution of the Western Cordiller. *Geol Soc Am Bull* 117, doi:10.1130/B25443.1.

Starke, V., Kirschtein, J., Fogel, M.L., and Steele, A. (2013) Microbial community composition and endolith colonization at an Arctian thermal spring are driven by calcite precipitation. *Environ Microbiol Rep* 5:648–659.

Staudigel, H. and Hart, S.R. (1983) Alteration of basaltic glass: mechanisms and significance for the ocean-seawater budget. *Geochim Cosmochim Acta* 47:337–350.

Staudigel, H., Furnes, H., Banerjee, N.R., Dilek, Y., and Muehlenbachs, K. (2006) Microbes and volcanoes: a tale from the oceans, ophiolites and greenstone belts. *GSA Today* 16, doi:10.1130/GSAT01610A.

Staudigel, H., Furnes, H., McLoughlin, N., Banerjee, N.R., Connell, L.B., and Templeton, A. (2008) 3.5 billion years of glass bioalteration: volcanic rocks as a basis for microbial life? *Earth-Science Reviews* 89:156–176.

Stern, J.C., Sutter, B., Freissinet, C., Navarro-Gonzalez, R., McKay, C.P., Archer, P.D., Jr., Buch, A., Brunner, A.E., Coll, P., Eigenbrode, J.L., Fairen, A.G., Franz, H.B., Glavin, D.P., Kashyap, S., McAdam, A.C., Ming, D.W., Steele, A., Szopa, C., Wray, J.J., Martin-Torres, F.J., Zorzano, M.-P., Conrad, P.G., Mahaffy, P.R., and the MSL Science Team. (2015) Evidence for indigenous nitrogen in sedimentary and aeolian deposits from the Curiosity rover investigations at Gale Crater, Mars. *Proc Natl Acad Sci USA* 112:4425–4420.

Stroncik, N.A. and Schmincke, H.-U. (2001) Evolution of palagonite: crystallization, chemical changes, and element budget. *Geochem Geophys Geosys* 2, doi:10.1029/2000GC000102.

Stroncik, N.A. and Schmincke, H.-U. (2002) Palagonite—a review. *Int J Earth Sci* 91:680–697.

Summons, R.E., Amend, J.P., Bish, D., Buick, R., Cody, G.D., Des Marais, D.J., Dromart, G., Eigenbrode, J.L., Knoll, A.H., and Sumner, D.Y. (2011) Preservation of martian organic and environmental records: final report of the Mars Biosignature Working Group. *Astrobiology* 11:157–181.

Tesdal, J.-E., Galbraith, E.D., and Kienast, M. (2013) Nitrogen isotopes in bulk marine sediment: linking seafloor observations with subsurface records. *Biogeosciences* 10:101–118.

Teunissen, E.H., Van Santen, R.A., Jansen, A.P.J., Drijneveldt, F.B. (1993) NH4+ in zeolites: coordination and solution effects. *J Phys Chem* 97:203–210.

Thorseth, I., Furnes, H., and Tumyr, O. (1995) Textural and chemical effects of bacterial activity on basaltic glass: an environmental record: final report of the Mars Biosignature Working Group. *Astrobiology* 11:157–181.

Torsvik, T., Furnes, H., Muehlenbachs, K., Thorseth, I.H., and Tumyr, O. (1998) Evidence for microbial activity at the glass-alteration interface in oceanic basalts. *Earth Planet Sci Lett* 162:165–176.

Towell, D.G. and Basu, A. (1999) Zeolite cement in martian volcanioclastic rocks [abstract 6149]. In *Fifth International Conference on Mars*, Lunar and Planetary Institute, Houston. H.-U., and Köster, H.M. (1986) Expanding behaviour, structural disorder, regular and random irregular interstratification of 2:1 layer-silicates studied by high-resolution images of transmission electron microscopy. *Clay Miner* 21:827–859.
van Zuilen, M. (2007) Stable isotope ratios as a biomarker on Mars. *Space Sci Rev* doi:10.1007/s11214-007-9268-1.

Wacey, D., McLoughlin, N., Saunders, M., and Kong, C. (2014) The nano-scale anatomy of a complex carbon-lined microsome in volcanic glass from the ~92 Ma Troodos ophiolite, Cyprus. *Chem Geol* 363:1–12.

Walton, A.W. and Schiffman, P. (2003) Alteration of hyaloclastites in the HSDP 2 Phase 1 Drill Core 1. Description and paragenesis. *Geochem Geophys Geosyst* 4, doi:10.1029/2002GC000368.

Westall, F., Foucher, F., Cavalazzi, B., de Vries, S.T., Nijman, W., Pearson, V., Watson, J., Verchovsky, A., Wright, L., Rouzaud, J.-N., Marchesini, D., and Anne, S. (2011) Volcaniclastic habitats for early life on Earth and Mars: a case study from ~3.5 Ga-old rocks from the Pilbara, Australia. *Planet Space Sci* 59:1093–1106.

Wilson, D.S. (1996) Fastest known spreading on the Miocene Cocos-Pacific plate boundary. *Geophys Res Lett* 23:3003–3006.

Wilson, D.S., Teagle, D.A.H., Acton, G.D., Alt, J.C., Banerjee, N.R., Barr, S.R., Coggon, R., Cooper, K.M., Crispini, L., Einaudi, F., Jiang, S., Kalberkamp, U., Kerneklian, M., Laverne, C., Nichols, H.J., Sandwell, R., Tartarotti, P., Umino, S., and Ziegler, C. (2003) *Proceedings of the Ocean Drilling Program, Initial Reports*, Vol. 206, edited by L.L. Peters, Ocean Drilling Program, College Station, TX.

Wilson, D.S., Teagle, D.A.H., Alt, J.C., Banerjee, N.R., Umino, S., Miyashita, S., Acton, G.D., Anna, R., Barr, S.R., Belghoul, A., Carlut, J., Christie, D.M., Coggon, R.M., Cooper, K.M., Cordier, C., Crispini, L., Durand, S.R., Einaudi, F., Galli, L., Gao, Y., Geldmacher, J., Gilbert, L.A., Hayman, N.W., Herrero-Bervera, E., Hirano, N., Holter, S., Ingle, S., Jiang, S., Kalberkamp, U., Kerneklian, M., Koepke, J., Laverne, C., Vasquez, H.L., Maclellan, J., Morgan, S., Neo, N., Nichols, H.J., Park, S.H., Reichow, M.K., Sakuyama, T., Sano, T., Sandwell, R., Scheibner, B., Smith-Duque, C.E., Swift, S.A., Tartarotti, P., Tikku, A.A., Tominaga, M., Veloso, E.A., Yamazaki, T., Yamazaki, S., and Ziegler, C. (2006) Drilling to gabbro in intact ocean crust. *Science* 312:1016–1020.

Wittmann, A., Korotev, R.L., Jolliff, B.L., Irving, A.J., Moser, D.E., Barker, I., and Rumble, D. (2015) Petrography and composition of martian regolith breccia meteorite Northwest Africa 7475. *Meteorit Planet Sci* 50:326–352.

Wong, M.H., Atreye, S.K., Mahaffy, P.N., Franz, H.B., Melson, C., Trainer, M.G., Stern, J.C., Conrad, P.G., Manning, H.L.K., Pepin, R.O., Becker, R.H., McKay, C.P., Owen, T.C., Navarro-Gonzalez, R., Jones, J.H., Jakosky, B.M., and Steele, A. (2013) Isotopes of nitrogen on Mars: atmospheric measurements by Curiosity’s mass spectrometer. *Geophys Res Lett* 40:6033–6037.

Wyatt, M.B. and McSween, H.Y., Jr. (2006) Orbital search for altered materials on Mars. *Elements* 2:145–150.

Zerkle, A.L. and Mikhail, S. (2017) The geobiological nitrogen cycle: from microbes to the mantle. *Geobiology* 15:343–352.

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**Abbreviations Used**

| Abbreviation | Description |
|--------------|-------------|
| 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 |