Nitrogenous Altered Volcanic Glasses as Targets for Mars Sample Return: Examples From Antarctica and Iceland

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Abstract  Mars exploration is focused on seeking evidence of habitable environments and microbial life. Terrestrial glassy basalts may be the closest Mars-surface weathering analog and observations increasingly indicate their potential to preserve biogeochemical records. The textures, major and trace element geochemistry, and N concentrations and isotopic compositions of subaerial, subglacial and continental lacustrine hyaloclastites from Antarctica, Iceland, and Oregon, respectively, were studied using micro-imaging and chemical methods, including gas-source mass spectrometry. Alteration by meteoric-sourced waters occurred in circum-neutral, increasingly alkaline low-temperature conditions of ∼60°C–100°C (Iceland) and ∼60°C–170°C (Antarctica). Incompatible large ion lithophile element (LILE) enrichments compared to mid-ocean ridge basalt (MORB) are consistent with more advanced alteration in Antarctic breccias consisting of heulandite-clinoptylilolite, calcite, erionite, quartz, and fluorapatophyllite. Granular and tubular alteration textures and radial apatite represent possible microbial traces. Most samples contain more N than fresh MORB or ocean island basalt reflecting enrichment beyond concentrations attributable to igneous processes. Antarctic samples contain 52–1,143 ppm N and have δ15N values of −6.7‰ to +7.3‰. Correlations between alteration extents, N concentrations, and concentrations of K2O, other LILEs, and Li and B, reflect the siting of secondary N likely as NH4+ replacing K+ and potentially as N2 in phyllosilicates and zeolites. Although much of the N enrichment and isotope fractionation presented here is not definitively biogenic, given several unknown factors, we suggest that a combination of textures, major and trace element alteration and N and other isotope geochemical compositions could constitute a compelling biosignature in samples from Mars’ surface/near-surface.

Plain Language Summary  Finding evidence of past or present life beyond Earth involves identifying physical features and/or chemistries preserved within rocks. Our knowledge of how the signs of life are preserved, and how to identify them, depends on our understanding of Earth biology and how similar rocks on other planetary bodies can preserve such evidence. Volcanic rocks containing natural glass that are subject to chemical modification by waters are relevant to studying alteration at/near the surface of Mars. We have analyzed examples from Iceland and Antarctica to identify textures, minerals, and chemistry, particularly nitrogen, because it is required for all life on Earth, and other elements that can become concentrated in minerals during rock alteration. Minerals formed as a result of rock-water interactions indicate their formation in fluids with pH < 9 and temperatures of <170°C. Relatively high concentrations of nitrogen correlated with those of other elements (i.e., potassium) indicate that nitrogen is stored in these minerals. Although much of the N chemistry here is not definitively the result of biological activity, chemically modified glassy volcanics containing nitrogen-bearing minerals may be useful targets to aim for, especially with other observations, when selecting samples on Mars in the search for ancient or modern life.

1. Introduction

Returning geological and atmospheric samples from Mars to Earth and detection of ancient or recent habitable environments and life are currently two of the most important objectives in planetary science. The Mars 2020 mission represents the initial step in sample-return as it entails scientifically selecting a set of ∼35 rock and soil samples that will be cached on the surface for future return to Earth. The challenge of detecting the widely
varying combination of potential organic, chemical, mineralogical and textural distributions that could constitute compelling signs of life and/or habitable paleoenvironments can only be met by (a) selecting appropriate sample targets with the potential to preserve evidence of surface-subsurface environmental and biological processes and (b) employing and integrating an equally wide variety of analytical techniques. An approach worth considering for this and possible future missions may be collectively employing the notions of “follow the water” (Briggs, 2000), “follow the glass” (Cannon & Mustard, 2015), and “follow the nitrogen” (Capone et al., 2006). We have addressed this set of suggestions through a detailed study of hydrous volcanic glass alteration in three Mars-analog terrestrial settings aimed at developing compelling biosignatures in these glasses.

The weathering of basaltic volcanic rocks has long been considered analogous to processes operating on the ancient or modern Mars surface (e.g., Gooding, 1978; Gooding & Keil, 1978). The past 40 years of telescopic, orbital spectroscopic, and in situ lander and rover exploration of Mars have revealed that most of the planet’s upper crust is basaltic/mafic in composition (Bandfield et al., 2000; Ehlmann & Edwards, 2014; Gregg & Williams, 1996; Schmidt et al., 2014; Poulet et al., 2007; Singer et al., 1979; Squyres et al., 2007; Vaniman et al., 2014) and primarily volcanic. A significant proportion of the surface materials may also be derived from hydrovolcanic activity, that is, where lava or magma interact with external liquid water or ice at or near a planetary surface producing glassy fragmental (hyalo-clastite) deposits (Fishers & Schmincke, 1984; Jones, 1966, 1969; Sheridan & Wohletz, 1983; Wohletz, 1983). Widespread on the Mars surface is an amorphous silicate phase possibly containing a non-crystalline alteration product such as palagonite (Chevrier et al., 2007; Evans et al., 1980; Horgan & Bell, 2012; Michalski et al., 2005). Also abundant are hydrovolcanic geomorphologies that include rootless cones, hyalo-clastite ridges, tuyas, and pyroclastic rock textures in locations such as Athabasca Valles, Pavonis Mons, and Chryse/Acidalia Planitia, and Home plate, Gusev crater (Fagents & Thorodson, 2007; Head & Wilson, 2007; Jaeger et al., 2007; Martinez-Alonso et al., 2011; also see Keszhelyi et al., 2010 and references therein). Together, these observations indicate the abundance of hyalo-clastites, with some of the glassy material likely produced by impacts.

Hydrothermally or low-temperature fluid-altered rocks have been regarded among the highest priority targets most likely to contribute to fulfilling scientific aims such as understanding Mars’ geologic surface processes, planetary evolution and its atmosphere, or the potential for life and its pre-biotic context (McLennan et al., 2012). There is growing evidence that altered modern and ancient terrestrial submarine, subaerial-lacustrine or subglacial pillow lavas, glassy basaltic breccias, and hyalo-clastite tuffs exhibit ample astrobiological potential (Bebout et al., 2018; Cousins et al., 2009; Furnes et al., 2008; Grosch & Hazen, 2015; Izawa et al., 2010; M. R. Fisk & Giovannoni, 1999; Nikitczuk et al., 2016; Staudigel et al., 2008). Various authigenic phases form during basalt weathering (Stroncik & Schmincke, 2001, 2002), several of which such as clays and zeolites reflect aqueous formation conditions and can provide useful biosignatures. Such lithologies are also habitable to microbes, which can play an important bio-catalyzation role in low temperature/hydrothermal basaltic glass alteration processes (Giovannoni et al., 1996; Thorseth et al., 1992, 1995, 2001; Torsvik et al., 1998) and thus can potentially incorporate and preserve objects, substances and/or patterns indicative of biogeochemical processes. A range of minerals has been identified on Mars commonly associated with altered basaltic igneous rocks, including those listed above, particularly Fe/Mg smectites such as nontronite, in addition to primary igneous minerals such as feldspar, clinopyroxene, and olivine (Ehlmann & Edwards, 2014; Grotzinger et al., 2014; Vaniman et al., 2014). Also, the occurrence of alteration minerals and X-ray amorphous materials in sedimentary rocks such as fluvio-lacustrine mudstones in Gale Crater (Bristow et al., 2018; Grotzinger et al., 2014; Vaniman et al., 2014), detrital olivine and Fe/Mg smectites in sedimentary fan deposits in Jezero Crater (Goudge et al., 2015), or aeolian sand dunes with high volcanic glass contents and detrital primary feldspathic minerals in the northern lowlands (De Vet et al., 2014) emphasize that many of the readily accessible sedimentary deposits on Mars contain primary and secondary minerals derived from volcanic or impactite deposits. Hyalo-clastites may hence be important targets for Mars sample return.

Several previous studies of variably palagonitized volcanic glasses from ocean basalts from the modern seafloor and (on land) Mesozoic ophiolite exposures presumed to have been altered on the ancient seafloor have shown that they can be concentrated in N (up to 18 ppm) and that sedimentary/organic N isotope signatures may be incorporated into associated authigenic phases via pore fluids during glass alteration (Bebout et al., 2018; Busigny et al., 2005a, 2005b; L. Li et al., 2007). Such observations are particularly important given the link between N and life on Earth (Fogel & Steele, 2013), the biogeochemical speciation behavior of N (Bebout et al., 2013; Busigny...
& Bebout, 2013), and the markedly lower N concentration (~0.2 mbar) and $^{15}$N-enriched isotope composition (+740‰) of the Martian atmosphere relative to the atmosphere of Earth (Mahaffy et al., 2013; Nier & McElroy, 1976; Owen et al., 1977; Wong et al., 2013). These observations regarding the Mars atmosphere have prompted some to ask, “Where is the nitrogen on Mars?” (see Mancinelli & Banin, 2003). Previous investigation of modern and ancient terrestrial basalt alteration and associated N contents and isotope compositions has been focused on those erupted in oceanic/sea floor environments (Bebout et al., 2018; Busigny et al., 2005a, 2005b; L. Li et al., 2007). Geomorphological and sedimentological observations, however, are more evident of fluviolacustrine and subglacial volcanic environments distributed across the Mars surface (Chapman, 2003; Galofre et al., 2020; Groitzinger et al., 2014, 2015; Smellie & Chapman, 2002). Thus, we have expanded this line of inquiry to include terrestrial lacustrine and subglacially to subaerially erupted basaltic and basaltic-andesitic hyaloclastites from Antarctica, Iceland, and Oregon. We consider a potential combination of textural and geochemical tracers (including major and trace element and silicate N isotope data) that could serve as compelling evidence of past and modern environmental and biological processes in hyaloclastites on other planetary bodies such as Mars.

2. Geologic Setting of Sampling Localities

2.1. Carapace Nunatak, Antarctica

The Kirkpatrick Basalts are part of the Jurassic Ferrar magmatic province, which consists of tholeiitic flood basalt lavas with minor pyroclastics, dolerite sills and dikes (Ferrar Dolerites) and the Dufek intrusion and was generated during the break-up of the supercontinent Gondwana in the largest preserved continental rift-related event in Earth’s history. The Kirkpatrick Basalt is a thick (300 m) sequence of predominantly subaerial, middle Jurassic (Heimann et al., 1994) hyaloclastite breccia with pillows consistent with being formed as a product of extrusive lavas flowing laterally into surface lake water (Ballance & Watters, 1971; Bradshaw, 1987). The base of the Kirkpatrick Basalt conformably overlays 130 m of cross-bedded lithic quartzose sandstone interbedded with fine conglomerates and mudstones (Carapace Sandstone; sample Carapace Sst, IGSN: IEAIO0004) consisting of detritus largely from a volcanic protolith (see Cannon et al., 2015). The exposed 430 m stratigraphic section located in the Transantarctic Mountains (Victoria Land), Antarctica is known as the Carapace Nunatak (Figure 1a). Samples KBH17 (IGSN: IEAIO0001), CPN1 (IGSN: IEAIO0002), and CPN2 (IGSN: IEAIO0003) examined in this study are coarse-grained palagonitized hyaloclastite flow-foot breccias retrieved from the Kirkpatrick Basalt, on two of which (KBH17 and CPN2) in situ micro-analytical work was focused.

2.2. Eastern and Western Volcanic Zones, SW Iceland

Iceland is situated in a magmatically, tectonically and geothermally active area that sits across the divergent Mid-Atlantic Ridge (Pálsson & Sæmundsson, 1974) and above a mantle plume (Schilling, 1973, 1975). Middle to upper Pleistocene (0.12–0.8 to <0.12 Ma) basaltic hyaloclastites were collected from ridges (tindars) and tuyas throughout southwest Iceland (Jakobsson & Gudmundsson, 2008; Jones, 1970; Kjartansson, 1943, 1960; Pedersen et al., 2020) in the Eastern and Western Volcanic rift zones (Figure 1b). These vitreous, clastic rocks formed during subglacial volcanic eruptions melting pre-existing ice sheets from beneath producing water-filled cavities where pillows, breccias, and tuffs sequentially accumulated (Gudmundsson, 2005; Gudmundsson et al., 2002; Jones, 1969, 1970; Smellie, 2005, 2006, 2007). Eruptions that melted through the ice (intraglacial) resulted in explosive sub-aqueous to sub-aerial hydrovolcanism and normal lava flows, respectively, some of which are visible capping deposits (Jones, 1969, 1970). A subset of two samples chosen for in situ micro-analyses are lithic to vitric tuff breccias from tuyas and fissure swarms of Laugarvatnsfjall and Reykjafell, respectively.

Sample LAU1 (IGSN: IEAIO0005) was collected from the Laugarvatnsfjall area (Jakobsson & Johnson, 2012; Jones, 1969, 1970) located NE of the Hengill volcanic center (Figure 1b). Observed near-base pillow remnants with mainly glassy vitric fragmental tuffs above, abundant lava clasts, the relatively steep sided mound-like profile typical of tuyas and relation to other linear ridges (tindars) indicate these are intraglacial volcanic rocks of the “Moberg Formation” (Kjartansson, 1959). The sequence of rock types and morphology are indicative of a growth sequence through an effusive aquatic phase into local bodies of up to 1,000 m deep water present during volcanism inferred to have been derived from the melting of ice by volcanic heating, followed by an emergent explosive and aerial effusive phases (Jones, 1969).
**Figure 1.** (a) Map of Antarctica showing the generalized distribution of Ferrar rocks, to which the Kirkpatrick Basalts belong, and the locations of Kirkpatrick Basalt outcrops in the central Transantarctic Mountains, including the Carapace Nunatak (after Siders & Elliot, 1985), the sampling location for hyaloclastite breccias used in this study. For a geologic map of the Carapace Nunatak, see Bradshaw (1987). (b) Map of Iceland showing the sampling locations for hyaloclastite tuffs used in this study. A generalized outline of upper Pleistocene “moberg” formations is represented in orange and the locations of the axial rift zones are also included (WVZ: Western volcanic zone; EVZ: Eastern volcanic zone; SISZ: South Iceland Seismic zone—after Jóhannesson and Sæmundsson (1998). The locations of Laugarvatn region and Reykjafell from which samples LAU1 and REY2 were collected are also indicated. Note. All samples collected fall within the orange outlined area and are <0.12 Ma. (c) Major volcanic rock chemical classifications of glass shards (EPMA) and whole rock (ICP-OES/ICPMS/XRF) hyaloclastites collected from Iceland, Antarctica (Kirkpatrick Basalts) and Fort Rock, Oregon based on total alkali-silica diagram after (Le Maitre, 1984) and (Le Bas et al., 1986). Alkalic-tholeiitic division is from Macdonald and Katsura (1964). Also plotted are Herdubreid Iceland tuff glass compositions (Stroncik & Schmincke, 2001), Mesa Range, Antarctica Kirkpatrick Basalts (Siders & Elliot, 1985) and DSDP/ODP Site 801 altered oceanic crust (L. Li et al., 2007). Most whole-rock analyses for this study were obtained using ICP-OES/ICPMS, some of which are reported without loss-on-ignition and are indicated with an arrow. (d) Patterns of incompatible rare earth elements for Iceland, Antarctic, and Oregon whole-rock hyaloclastites and separates normalized to mid-ocean ridge basalt values of McDonough and Sun (1995). Whole-rock and in situ major and trace element data plotted in panels (c and d) can be accessed here: https://doi.org/10.26022/IEDA/112220 (Nikitczuk et al., 2022).
The REY2 (IGSN: IEAIO0006) subglacial hyaloclastite was collected from the Reykjafell mini-graben structure (Hardarson et al., 2015) located along the western flank of the Western Volcanic Zone's (see Jakobsson & Johnson, 2012) Hengill central volcano, which hosts a significant geothermal system (Hellisheiði high temperature field) of Iceland. This area is dominated by NE-SW striking faults and fissure swarms, which control the NNE-SSW graben orientation. Geophysical mapping and temperature logs indicate that Reykjafell is located above one of at least three geothermal up flow zones related to <10 ka hyaloclastite fissures, the highest temperatures of which are recorded at Reykjafell (Hardarson et al., 2015; Helgadóttir et al., 2010).

2.3. Basaltic Tuffs From the Fort Rock Volcanic Field, Central Oregon, USA

Samples FR-12-97E and FR-12-107 were collected from the Reed Rock and The Black Hills subaerial continental lacustrine hydrovolcanic tuffs rings, respectively. They formed by subaerial eruption through the Pliocene-Pleistocene (646–23.2 ka) pluvial Fort Rock Lake in saline, neutral to alkaline waters. A more detailed description of the area and the sampling locations is provided by Nikitczuk et al. (2016) and Nikitczuk (2015). Also see Heiken (1971).

3. Materials and Methods

We examined a sample suite consisting of 4 Antarctic (1 sandstone), 15 Iceland, and 2 Oregon hyaloclastites. These were selected because they can serve as analogs to early Mars surface/near-surface low temperature to hydrothermal weathering of glassy basaltic volcanics (e.g., Ehlmann & Edwards, 2014 and references therein). A variety of analytical techniques were performed at (a) the Lehigh University, (b) the Pheasant Memorial Laboratory (PML), Institute for Planetary Materials, Okayama University, (c) The University of Western Ontario, and (d) Activation Laboratories (Ancaster, Ontario). A subset of two samples each was selected from the Antarctic and Iceland suites for in situ micro-analyses (Figure 2) based on grain size and the presence of fresh glass.
secondary phases, and alteration textures. All microanalytical work was performed on 2.5 cm diameter round polished 30–50 μm thick petrographic thin sections whereas other geochemical analyses were conducted on whole-rock or physical separates.

Methods applied include (a) identification and characterization of microtextural features and phases using optical microscopy under plane, cross polarized and reflected light (see example images in Figures 2 and 3), (b) high magnification observations using field emission scanning electron microscopy (SEM), (c) determining major and trace element compositions and distributions with whole rock and in situ microprobe methods such as ICP-OES/ICPMS, PGNAA, XRF, EDS, WDS (EPMA), and SIMS (for Li and B), (d) whole-rock and in situ phase identification using pXRD, μXRD, and Raman spectroscopy, and (e) measurements of N concentrations and isotopic compositions (expressed as δ15Nair) using a system developed by Bebout et al. (2007, 2018; L. Li et al., 2007) for analyzing nanomole quantities of N2 by sealed tube combustion and carrier gas methods (GC-IRMS). The Supporting Information S1 contains more detailed descriptions of the methods listed above, where appropriate including discussion of standard materials used for elemental analyses and analytical conditions.

4. Results

4.1. Textural and Mineralogical Observations

Antarctic hyaloclastite flow-foot breccias consist of clast supported, angular lapilli-sized, nearly avesicular, fractured glass fragments and shards (Figures 2a and 2b). Primary igneous minerals include plagioclase, clinopyroxene, titanomagnetite and pyrite as glomerocrysts and phenocrysts and rare microlites. Glass alteration ranges from nearly fresh to completely replaced by secondary silicates in 50 μm to 1 mm-wide irregular alteration zones and all clast margins have smectite-rich coatings, usually exhibiting a zonation (Figures 3a–3c). Hollow and/or mineralized tubular and elongate oriented clay-filled features (Figure 3d and Figure S1 in Supporting Information S1) and 0.1–1 μm amalgamated granules are present at interfaces between fresh glass and altered zones and along fractures. No smooth banded alteration fronts exist. Fine-grained secondary pyrite is present along smectite layer interfaces and radial nontronite-apatite geo-petals after heulandite-clinooptilolite cements are also present (see the Mg-rich portions in Figure 3c). Intergranular pores (mm to cm-scale) and vesicles connected to clast exteriors via fractures are infilled with smectites nontronite-saponite, zeolites heulandite-clinoptilolite and erionite, hydroxy- and fluorapophyllite, calcite and quartz. Acicular erionite crystals are embedded within late quartz (Figure 3a). Micro and powder XRD (Figures 4a and 4b), Raman spectroscopy (Figures 4c and 4d), and major element chemistry (Figures 4e–4j) confirm authigenic and primary phases. See the Supporting Information S1 for more detailed petrographic description.

Iceland subglacial hyaloclastite tuffs consist of subrounded to blocky subangular, vesicular, moderately fractured, mainly matrix-supported, porphyritic, glassy fine to coarse ash and lapilli sideromelane and lava clasts (Figures 2c–2f) with phenocrysts and glomerocrysts of olivine, plagioclase, clinopyroxene, and sparsely opaques. Hopper olivine with glass inclusions, swallowtail plagioclase, undercooling and crystal fragments occur throughout the matrices. Degrees of glass alteration range from fresh to completely palagonitized (ash fragments) typically with 2–20 μm-wide zones of yellow amorphous palagonite and smooth or irregular fronts (Figures 3g–3i). Glass-alteration interfaces contain hemispherical amalgamations of 0.2–0.5 μm granular pits and/or hollow tubules extending into fresh glass (Figures 3i, 3k and 3l and Figure S1 in Supporting Information S1). Multi-layer alteration is variably present. Grains surfaces are coated in 10–20 μm thick, sometimes multi-layer, mixed smectites with small vesicles infilled. Radial 10–20 μm diameter or ~1 μm angular apatite mineralizations are embedded in smectite coatings (Figure 3j). Chabazite, thomsonite, or calcite cements infill vesicles usually on smectite coatings. Secondary 0.1–0.5 μm pyrite grains exist along smectite coating interfaces or along vesicle surfaces. The smectites saponite, nontronite and montmorillonite, the zeolites chabazite and thomsonite, calcite and apatite are confirmed by μXRD, Raman and major element chemistry (Figure 4).

4.2. Major and Trace Element Chemistry of Whole Rock, Separates, and Glasses

Figures 1c and 1d display major and trace element data of Antarctic and Iceland-Oregon whole-rock/separates and glasses of select Antarctic-Iceland samples and their classification based on total alkali versus silica. Antarctic hyaloclastites are basaltic andesitic to andesitic tholeiites containing 53.97–64.9 wt. % SiO2, the higher concentration in the quartz-bearing Carapace Sandstone. Samples KBH17 and CPN2 have fresh glass averages of
Figure 3. Photomicrographs of Antarctica (a–f) and Iceland (g–l) hyaloclastites. (a) Lapilli breccia clast with fresh glass core, ~0.5 mm wide alteration zone, smectite coating, zeolite, apophyllite, and quartz cements. This area was mapped for major elements (Figure 5a). (b) A zeolite filled vesicle at left coated in smectites, and glass that has been completely replaced with smectites and a Ca-K-zeolitic phase. A dark fracture runs from top to bottom of image along which a smectite-rich zone has formed (darker orange area). Fresh plagioclase phenocrysts are also visible. (c) Back-scattered electron (BSE) image across an altered and cemented Antarctic breccia clast in sample KBH17 overlayed with a Mg element map generally showing an increase in Mg away from glass surface. This area is similar to that indicated at higher magnification in panel (a). The fresh glass core is located toward the top right of the image, which grades toward the lower left into an irregular alteration front consisting of elongate dissolution channels, sparse micro-tunnels, and a patchwork of smectite after zeolitic glass replacement. The exterior is coated in a layer of nontronitic smectite, the very outer layer of which shows a drop in Mg concentration due to significant decrease in density (increase in porosity) which grades into smectite-apatite geo-petals within a heulandite-clinoptilolite cement. (d) BSE image of a similar location to that in panel (c) showing an irregular alteration front with elongate dissolution channels (arrow) infilled with nontronite extending from the glass margin where the glass nearest to margin has been replaced by and the exterior coated in smectites. (e) Plane polarized light image of a long simple tunnel with rough spiral-like surface within fresh Antarctic glass in an irregular alteration front. (f) Various rounded to oblong cross sections of clay-filled micro-tunnels. (g) Plane polarized image of amorphous palagonitized glass with exterior vesicle surface coated in saponitic smectites followed by thomsonite zeolite cement. (h) Altered glass with zoned amorphous palagonite with a granular alteration front. The vesicle is also coated in smectites with the very center of the pore infilled with thomsonite. See Figure 5c for major element maps of an area showing similar smectite-zeolite paragenetic relationship as shown in panels (g and h). (i) BSE image overlayed with a Mg element map displaying a chemical zonation. The vesicle is coated in multilayered smectite. (j) Radial apatite mineralization embedded within smectite coating. (k) Simple, smooth, tapered tunnels radiating from a vesicle (right arrow) and a central point at high angles to a fracture surface (left-center). (l) Smectite-filled vesicles and amorphous dual-zone palagonite grading into a fine granular alteration front. This area is like that at higher magnification in panel (h). Labels are: ap: apophyllite; apt: apatite; cl: clinoptilolite; c: coating; et: erionite; gr: granular alteration; hl: heulandite; pl: plagioclase; qtz: quartz; pal: palagonite; sm: smectite; tb: tubules; th: thomsonite; V: vesicle; and zl: zeolite).
Figure 4. Micro X-ray diffractograms (a and b), Raman spectra (c and d) and WDS spot analyses (e–j) of Antarctic (KBH17 and CPN2) and Iceland (LAU1 and REY2) secondary phyllosilicates and zeolites. Phyllosilicates as smectites and fresh glass formulas were calculated on the basis of 22 oxygen, with all iron as FeO. Fresh glass points are averages for each sample. For panels (a and b), the black patterns from angles of ∼4°–97° 2θ depict omega scan detections whereas the blue stacked patterns from ∼3° to 52° 2θ display the off-coupled scans that can re-produce characteristic clay peaks at the very low 2θ angles typically only identifiable with pXRD. Diffractogram in panel (b) displays an “amorphous hump” from 15° to 40° 2θ produced mainly by the glass component and subordinately probably by the non-crystalline palagonite component. Background subtractions were performed on all diffractograms. (c and d) The red spectra are the detected signals whereas the green-violet spectra are from the database used for identification. (e–i) The reference phyllosilicates nontronite, saponite, montmorillonite, beidellite, biotite, and muscovite are from Deer et al. (2013; and references therein) whereas berthierine is a glass replacement found in Martian Nakhla meteorite from Brindley (1982). (j) Plot of Si/Al versus (Na + K)/Ca ratios for chabazite and thomsonite from Laugarvatnsfjall and Reykjafell, Iceland, and heulandite-clinoptilolite and erionite from Kirkpatrick Basalt hyaloclastites of the Carapace Nunatak, Antarctica. In situ major element data plotted in panels (e–j) can be accessed here: https://doi.org/10.26022/IEDA/112220.
56.95–56.87 wt. % SiO₂. Iceland-Oregon samples are mainly low-K tholeiitic basalts containing 42.3–47.1 wt. % whole-rock SiO₂ (with LAU1 and REY2 having 45.35 and 43.51 wt. %, respectively). Iceland fresh glasses have averages of 47.05 wt. % (LAU1) and 47.32 wt. % (REY2) SiO₂. Total Fe as Fe₂O₃ wt. % ranges from 8.76 to 16.19 in basalts and 0.03–12.29 in Antarctic samples. Whole-rock-Fe₂O₃ (T) wt.% (Antarctic: 10.69–12.44 and Iceland: 11.3–11.68) are slightly higher than but agree with total Fe as FeO wt. % of fresh glasses (10.78–10.83 and 10.64–10.98, respectively). MgO and CaO wt. % in basaltic tuffs range from 4.3 to 12.59 and 6.5 to 11.19, respectively. Iceland samples LAU1 and REY2 have MgO and CaO wt. % of 7.2 and 9.59, and 9.49 and 7.89, respectively, whereas Antarctic separates range from 0.02 to 3.05 and 1.12 to 19.99, respectively, with the high CaO from cements. The range of K₂O wt. % is 0.03–1.65, the highest values being from the Carapace Sandstone and an alteration rind. TiO₂ in the Antarctic samples ranges from 0.002% (quartz cement) to 1.20% (alteration rind) whereas the basalts range from 0.735 wt. % to 3.96 wt. % with 1.68 and 1.76 in LAU1 and REY2, respectively. Boron concentrations in basalts range from 3.3 to 12.6 ppm and the Antarctic samples show the highest measured concentrations (26.4 ppm in the Carapace Sandstone and 16 ppm in an alteration rind). The quartz-bearing Carapace Sandstone also has higher SiO₂ wt. %. With respect to average fresh glass, Iceland tuffs contain lower SiO₂, TiO₂, Al₂O₃, MnO, CaO, and Na₂O and higher MgO, whereas the Antarctic whole-rock contains lower SiO₂, TiO₂, Al₂O₃, MnO, MgO, Na₂O, and higher K₂O. Iceland spectra most closely match phyllosilicate spectra whereas the Antarctic spectrum resembles those of zeolite cements (Figure 1d). Whole-rock and average glass compositions are found in Table S1 in Supporting Information S1 and the data set accessible at https://doi.org/10.26022/IEDA/112220 (Nikitczuk et al., 2022).

The mid-ocean ridge basalt (MORB)-normalized REE concentrations for basaltic whole-rock and basaltic andesitic whole-rock and separates are displayed in Figure 1d. All hyaloclastites and separates, except one Iceland sample, are enriched in light rare earth elements (LREE) and highly incompatible large ion lithophile elements (LILEs) Cs, Rb, Ba, Th, and U (listed in order of decreasing incompatibility) generally considered fluid mobile. Basalt LREE enrichments relative to the heavy rare earth elements are commonly observed in Iceland especially along the Reykjanes ridge (S. S. Sun et al., 1979; and references therein) and may be classified as “plume” (P)-type MORB (Schilling, 1975), which occur in various oceanic environments including intraplate islands such as Hawaii, mid ocean ridges, and ridge-straddling islands (i.e., Iceland). The Antarctic basaltic andesite samples are the most enriched in Cs relative to MORB. The Oregon tholeiitic basalts are least enriched in Nb followed by the Antarctic samples and FR-12-107 from Oregon shows a Nb depletion. The most pronounced, yet modest Eu anomalies are exhibited by the Antarctic samples. Samples LAU1 and REY2 show closely similar curves but LAU1 is less enriched in incompatible elements, including and LREEs. Compared to LAU1 and REY2, all the Antarctic samples are less enriched in Nb and more enriched in K₂O and show larger Eu anomalies. REE spectrum and trace element variation diagrams are consistent with the Antarctic samples belonging to the low-Ti flows of the Ferrar Group rocks suggested by Siders and Elliot (1985).

4.3. Major and Trace Element Chemistry of Secondary Textures and Minerals

Figure 5a displays a representative SEM image across an alteration zone in an Antarctic hyaloclastite (KBH17) and major elements maps corresponding to the area in Figure 3a. Zones of Ti, Fe, and Mg-enriched glass alteration, including elongate dissolution channels and tubular-granular textures, correspond to smectite (nontronite) replacement with Si, Al, Ca, Na and K all depleted with respect to fresh glass. Smectite coatings on clast margins and vesicles are generally more Ti and Mn-depleted but show similar depletions and enrichments of Fe, Mg, Si, Al, Ca, Na, and K although generally more Mg-rich than glass replacement. Most phyllosilicates have Mg/Mg + Fe ratios, Si + Al contents and octahedral totals that reflect the Fe-rich primary glass substrate and are consistent with mainly the Fe-smectite nontronite (Figures 4e–4i). Higher interlayer cation (Na + K + Ca) contents indicate that micas may represent part of the phyllosilicate assemblage (Figure 4b). Elevated B concentrations usually coincide with Li enrichment in secondary smectite-clay phases, but Li concentrations are consistently higher than those of B (see Figure 5b and Figure S5 in Supporting Information S1). Alteration zones also show intermingled regions of Si, Al and K enrichments with co-located Ca and Na corresponding to zeolitic replaced glass with compositions similar to those of cements (heulandite-clinoptilolite-erionite) and variable Li and B concentrations consistently lower than those of phyllosilicates. All (Na + K)/Ca ratios (Figure 4j) of zeolite cements are <1 and Si/Al ratios vary between 2.9 and 4.6 consistent with Ca-rich heulandite (<4.0) and clinoptilolite (>4.0) (Coombs et al., 1997). The glass replacement is comparatively more depleted in most
Figure 5.
elements though with the cements being more enriched in K and the glass replacement more K-depleted. Phosphorus co-enrichments with Ca and F are limited to fine grained apatite-smectite geo-petals along glass margins that smectite coatings grade into. Co-concentrated Ca, K, F and Si correspond to apophyllite cements whereas Ca enrichments also correspond to calcite with elevated B concentrations observed in both phases. Sulfur is concentrated in secondary fine-grained to framoidal pyrite along smectite layer interfaces or embedded within coatings, or as globular igneous pyrite. See Figures S2 and S4 in Supporting Information S1 for WDS spot analyses of authigenic phase compositions with respect to fresh glass represented as spidergrams and transects, respectively.

In Iceland tuffs, areas of amorphous glass alteration (palagonite) show depletions in Na, Mg, Ca, Al, Si, variable K, and Li concentrations and consistent co-enrichments in Ti and Fe with associated granular/tubular textures more Na and K-depleted and Mg-enriched but similarly B and Ti-enriched with respect to fresh glass (Figures 5c–5d). The highest B concentrations are associated with granular-tubular glass alteration and fine intergranular matrix materials. Concentrations of Mg, typically decreasing away from glass surfaces, with variably co-located Fe, Al and Si along glass margins and infilling vesicles correspond to smectite clays of mostly saponite composition but spanning Si + Al, Mg + Fe and octahedral cation totals (Figure 4) indicative of possible intergrowths of saponite-nontronite to montmorillonite (consistent with XRD analyses), illite and possibly beidellite. Low concentrations of interlayer cations suggest that micas are not a significant component. The Si and Al contents and Mg/Mg + Fe ratios reflect the primary substrate (sideromelane) compositions. Commonly smectite coatings showing high levels of Si that also coincide with elevated Li concentrations and elevated or depleted B with respect to fresh glass (Figure 5b and Figure 5d in Supporting Information S1). Concentrations of Ca-K-Al co-located with Si correspond to zeolite cements. The ratios of (Na + K)/Ca are mostly lower than 0.5 whereas Si/Al ratios range from 1.3 to 1.8 and are mainly chabazite (Figure 4j) generally showing Li and B concentrations to be minute or absent (Figure 5d). Calcium enrichments also correspond to calcite cements. High co-enrichments of Ca and P and variable S correspond to radial apatite embedded in smectite coatings whereas S and Fe co-enrichments are restricted to fine-grained pyrite along smectite layer interfaces (see S-map in Figure 5c). In what appears to be hydrated zones of early glass alteration, Li and Na are depleted.

4.4. Nitrogen Concentrations and Isotopic Compositions

The N concentrations and isotope compositions of Antarctic and Iceland hyaloclastites are presented in Figure 6. Nitrogen concentrations for whole-rock and physical separates of glass alteration and silica-zeolite cements from the hyaloclastite breccias of the Kirkpatrick Basalt at Carapace Nunatak range from 52 to 1,577 ppm with the highest and lowest concentrations exhibited by the alteration rind separates. The Antarctic samples also show strongly negative δ₁⁵Nₑₑₑₑ of −20.8‰ to −7.1‰. All Antarctic samples have N concentrations higher and δ₁⁵N values lower than those associated with fresh mid-ocean ridge or ocean island basalt (MORB, OIB). There is no apparent correlation between N contents and isotope values, but the alteration rind separate with the highest measured concentration also has the most negative δ₁⁵N value. The hyaloclastite tuffs from Iceland (and two from Oregon) have whole-rock N concentrations ranging from 1.6 to 172 ppm and δ₁⁵N values ranging from −6.7‰ to +7.3‰. Most of the whole-rock concentrations are higher than MORB or OIB glasses and have δ₁⁵N values more positive than fresh MORB and similar to OIB glass. Both samples subject to in situ analyses (LAU1, REY2) show the lowest measured concentrations (1.6 and 2.2 ppm, respectively) and most negative δ₁⁵N values (−5.0‰ and −3.3‰, respectively) that most closely resemble those of typical MORB values. No correlation is observed between the presence of putative microbial textures and N contents or isotope compositions.

Figure 5. Backscatter electron images, major elements, and Li-B of alteration assemblages from round polished 2.5 cm diameter petrographic thin sections of the Antarctic Kirkpatrick Basalt hyaloclastite breccia (a and b) and Icelandic Laugarvatnfsjall hyaloclastite tuff (c and d). Major element map colors represent relative concentrations for each individual element. The Li-B images are concentration maps (ppm). (a) Back-scattered electron (BSE) image corresponding to the area in Figure 3a. Bottom panels display WDS element maps. The K and Fe enrichments in the alteration zone correspond to zeolite and smectite glass replacement, respectively. (b) Antarctic cements show high Li concentration correlated with high B concentrations in smectites and the lowest Li concentrations in quartz cement. Heulandite also shows elevated Li concentrations compared to quartz, but lower B concentrations. (c) Top left panel shows a BSE image of a glassy, vesicular lapillus with the area mapped outlined by the white dashed box. The inset shows a plane-polarized photomicrograph of the same area with a white dashed box outlining the map area. The top right panel shows an enlarged BSE image of the map area. The Icelandic alteration assemblage displayed shows amorphous palagonite propagating inward from vesicle walls (yellow in plane polarized image), several vesicles coated with chemically zoned clays and/or infilled with chabazite cement, secondary apatite (top left of Ca-P-maps) and pyrite (see S-map). Bottom vesicle shows Mg-rich saponitic coating with later Ca-Al-Si-rich chabazite cement. (d) Glassy ash clasts with granular alteration, smectite coatings along margins (arrows) and intergranular chabazite cements. Granular alteration shows depleted Li and elevated B. See Figure 3 caption for label legend.
5. Discussion

5.1. Glass Alteration in Iceland Versus Antarctica

We note that, for the Antarctic samples, a main, initial alteration stage that included glass alteration and replacement (and mostly the formation of smectites and zeolites) was followed much later by another secondary alteration event involving apophyllite formation (see the discussion in Section 5.2.1). The key comparisons here with Iceland alteration are mainly with the earlier-stage alteration in Antarctic samples. The secondary mineral assemblages in diagenetically or hydrothermally altered vitric volcanic rocks tend to crystallize from thermodynamically unstable...
materials (e.g., glass and palagonite) to progressively more stable lower energy assemblages (through smectites, zeolites, and amorphous silica to quartz) with time and greater temperatures promote faster rates (Chipera & Apps, 2001; Dibble & Tiller, 1981). Therefore, crystallization during aging can indicate reaction progress or maturity of the alteration (Jakobsson, 1972; Jakobsson & Moore, 1986; Stroncik & Schmincke, 2001, 2002). A significant difference between the Antarctic hyaloclastite breccias and the Iceland-Oregon tuffs is the degree of crystallinity both as a direct product of glass alteration and as intergranular cements. If palagonite is to be considered only the amorphous product of glass alteration, as suggested by Stroncik and Schmincke (2001), then true (gel)palagonite is observed only in the Iceland-Oregon basaltic tuffs (Figures 3g–3i). A proto-crystalline alteration phase (i.e., fibro-palagonite), however, is only observed in the Oregon tuffs. Essentially all the altered glass within the Antarctic rocks consists of secondary minerals (e.g., Figure 3b). In KBH17 and CPN2 depletions in Na and Li are observed in zones adjacent to late fractures or within alteration zones. They are only visible in backscattered electron (BSE) images and are possibly a slightly hydrated precursor to palagonite. Depletions in Si, Al, Mg, Ca, Na, and K and enrichments of Ti and Fe (see Figures 5a–5c and Figures S2, S4 in Supporting Information S1) consistently observed in the Iceland samples relate to the formation of purely amorphous palagonite. Such element mobilities during the initial stage of alteration are commonly observed in various other examples of palagonite formation in basalts (Furnes, 1978; Walton et al., 2005; Zhou & Fyfe, 1989). The crystallinity of the Iceland (least altered/crystalline, ∼10 ka), Oregon (proto-crystalline glass alteration, 646–23.2 ka), and Antarctic (most altered/crystalline, ∼176 Ma) samples, especially the presence of late quartz cements and complete glass replacement with minerals in KBH17 and CPN2 alteration zones reflect the different stages of alteration process (Peacock, 1926; Stroncik & Schmincke, 2001, 2002; Zhou & Fyfe, 1989) that here correlate with eruption ages.

Although the Antarctic hyaloclastites are significantly older than the Iceland basalts (∼176 Ma vs. <0.12 Ma), they preserve large domains of fresh unaltered glass. This may reflect the larger grain sizes and cementation progressively reducing porosity and permeability, but the more felsic composition of the glass (Figure 1c) also likely played a role in the rate of alteration during the initial stages and subsequently thereafter. An important process that occurs during glass devitrification is the uptake of H2O, the catalyzing action of which acts to break O and Al bonds with Si. However, felsic glasses may require a greater degree of hydration before crystallization can initiate because they contain greater numbers of Si bonds (Bonatti, 1965; Marshall, 1961). The alteration process may thus have generally been slower. It is possible for felsic glasses to stay in a vitreous state for tens of millions of years (Forsman, 1984) as is evidenced by the presence of fresh glass cores in Antarctic samples KBH17 and CPN2. Mafic glasses, however, are thought to react with fluids more readily (Morgenstein, 1987).

The Iceland and Antarctic hyaloclastites display textural and chemical zonation reflecting the control that evolving fluid composition and pH had on their formation (Fisher & Schmincke, 1984; Furnes, 1975; Hay & Iijima, 1968; Thorseth et al., 1991). The accumulation and enrichment of Mg can also indicate reaction progress whereas the overall crystallinities highlight the difference in the degree of alteration. Palagonitized glasses often show zonation reflecting the continuous re-equilibration of the material being altered with the chemically evolving fluids (Crovisier et al., 1992). Most notable here are concentrations in Mg and to a lesser extent Al in palagonitic material (where multiple bands are visible) and in smectite coatings that increase outward and away from the glass surface, respectively. With increasing reaction progress the precipitating mineral species change with time as surface reactions control dissolution and in turn the dissolved species that reach solubility limits re-precipitate in thermodynamic equilibrium with the dissolving fluids (Crovisier et al., 1987, 1992). Porosity and permeability would also decrease, gradually closing the water-rock system (as evidenced by cementation), allowing less flow and fluid-rock interactions. Changes in water/rock ratios have large influences on the activities of major elements that are either fixed in secondary minerals or lost to solution (e.g., Si, Mg, Al, Ti, K, Na, and Ca). Iron, Ti, and Al are often considered to be insoluble during basalt-glass dissolution at near-neutral pH whereas Mg is mostly not. A change in fluid pH change during alteration is especially supported by the secondary minerals, mainly the zeolite assemblage (Figures 3–5) present in all samples (see the discussion below).

5.2. Source Water Composition and Alteration Conditions

The Iceland hyaloclastite tuffs were affected by meteorically sourced waters. Most were erupted in subglacial conditions, and to a lesser extent phreatomagmatic when intraglacially erupted, and affected by glacial melt waters and Iceland meteoric waters initially near 0°C. Typically the pH of the solutions produced from rain and snow melt in Iceland is 5–6 but upon atmospheric equilibration and initiation of water-rock interactions (e.g.,
dissolution and precipitation) solutions become increasingly alkaline (Gislason & Eugster, 1987). Surface waters sampled from geothermal NaCl, steam-heated-acid-sulfate and mixed surface waters across Iceland range from 4°C to 100°C (Kaasalainen & Stefánsson, 2012) with pH between 2.01 and 9.10. Based on the mineral assemblage, acid-sulfate waters did not affect these samples. Aquifer temperatures based on well logging also range from <40°C to 350°C (Kaasalainen & Stefánsson, 2012 and references therein) with typically neutral to alkaline pH. Given the subglacial-erupted nature of these deposits it is likely that heated surface waters most significantly influenced these samples rather than that from subsurface aquifers. Authigenic zeolite compositions have previously been used in subglacial hyaloclastites as geochemical indicators of water source types involved in their formation (Johnson & Smellie, 2007). The chemical compositions of Iceland zeolites (mainly chabazite) with (Na + K)/Ca ratios below 1.0 are consistent with formation from meteoric- rather than marine-sourced waters.

The rocks collected from Antarctica also erupted into meteoric (lake) waters connected to a regionally groundwater-rich source area related to a topographic basin that formed during the development of an Early Jurassic rift zone (Ballance & Watters, 2002; Hanson & Elliot, 1996). The Kirkpatrick Basalt at Carapace Nunatak has numerous fossil interbeds in its lower portions (Bradshaw, 1987) and conformably overlays the Carapace Sandstone, which includes fossiliferous chert lenses containing a diverse group of freshwater biota (Ballance & Watters, 1971; Gunn & Warren, 1962; Tasch, 1987; Yanbin, 1994) indicative of lake deposits. The volcanic environment during rifting in Antarctica during this time was envisioned by Gunn and Warren (1962) as “elevated and moderately rugged relief, and conditions similar to those in present day Iceland.”

Based on measurements from drill holes in various hydrothermal areas, solutions involved in zeolitization are generally alkaline and those that form Ca-silicate types have greater Ca concentrations (Utada, 2001). Petrographic relationships in both the Iceland-Oregon and Antarctic hyaloclastites where smectites coat exterior glass surfaces and zeolite cements coat smectites and infill pores (Figures 3a–3c, 3g, and 3h) indicate that smectite coating formation mostly preceded precipitation of zeolites. In KBH17 and CPN2, heulandite-clinoptilolite lines pores/margins of glass surfaces coated in nontronite-saponite, Chipera and Apps (2001) proposed that with increasing solution alkalinity, zeolite formation in more silicic glassy deposits (rhyolitic) favors clinoptilolite formation over smectites, consistent with observations here.

The alteration of the Iceland and Antarctic hyaloclastites is consistent with open system, low temperature, neutral to alkaline pH conditions. The zeolites clinoptilolite and chabazite are phases of the first to form in shallow open system rock-water interactions (Sheppard & Hay, 2001) and increasingly alkaline solutions tend to favor the stabilization of clinoptilolite (Chipera & Apps, 2001) and most other zeolites. In low temperature (<150°C) geothermal areas throughout Iceland, chabazite zones are associated with the lowest temperatures in the upper most 1 km whereas heulandite is one of the most common minerals observed in the higher temperature geothermal areas (>200°C; Kristmannsdóttir & Tómasson, 1978). Those zeolites are found in basaltic hyaloclastite and lava rock types that dominate those areas. Geothermal fluids of meteoric origin in Iceland typically have pH 9–10 measured at 20°C (Chipera & Apps, 2001). In Iceland samples LAU1 and REY2, the main zeolite identified is chabazite with thomsonite along with smectite (saponite-nontronite-montmorillonite), whereas the Antarctic samples KBH17 and CPN2 contain mainly heulandite-clinoptilolite and erionite along with smectites (nontronite-saponite). KBH17 and CPN2 also contain later silica (quartz) and calcite, respectively, but the erionite present formed later than heulandite-clinoptilolite in a more closed system environment after a significant amount of cementation had occurred. Erionite is not commonly observed in open hydrologic systems (Sheppard & Hay, 2001) and here is generally observed as embedded within later-formed quartz. Observations of secondary minerals in other hydrothermally altered Iceland basalts have shown the temperature distributions of chabazite (25°C to >75°C), thomsonite (~60°C to >100°C), heulandite (60°C to >150°C), smectites (nontronite, 25°C–200°C), calcite (0°C to >250°C), and quartz (<100°C–300°C) (Chipera & Apps, 2001; Apps, 1983). These suggest Iceland samples LAU1 and REY2 experienced overall lower alteration temperatures (60°C–100°C) compared to the Antarctic hyaloclastites KBH17 and CPN2 (60°C–170°C). Although the Reykjafell area (REY2) is known to be located within one of the most powerful geothermal fields of Iceland, formation temperatures inferred from well logging that indicate ~50°C–100°C agree with the low temperature zeolite zone hydrothermal alteration mineralogy (Helgadóttir et al., 2010). In both cases, smectite coatings were formed mostly at temperatures slightly higher than those during formation of the zeolite cements.
5.2.1. Secondary Heating Event in Antarctica (Apophyllite)

The textures and mineralogy indicate the Kirkpatrick Basalt hyaloclastites experienced multiple stages of alteration. Despite petrographic indications of the progressive sealing of the rock system by the precipitation of secondary minerals in pore spaces, later fracturing or faulting and separation of grain boundaries may have opened the system to fluid migration, alteration, and formation of additional secondary minerals. Combined data from $^{40}$Ar/$^{39}$Ar heating methods on feldspar and biotite separates have revealed that the episode of continental flood basalt magmatism that produced the Kirkpatrick Basalts occurred at $\sim$176 Ma ($176.6 \pm 1.8$, $176.8 \pm 0.5$, $176.4 \pm 0.4$, and $176 \pm 0.7$) within an interval of less than 1 m.y. (Fleming et al., 1997; Heimann et al., 1994). Apophyllite, which has been identified here and in previous studies in Antarctic hyaloclastites (Kirkpatrick Basalts) petrographically appears to have formed later than zeolites within the initial formation context and as later final cementation not related to the initial alteration stage. Although the conditions under which apophyllite is stable are not well-established, the phase typically forms paragenetically late and at temperatures of $<100^\circ$C (Kristmannsdóttir & Tómasson, 1978). Based on K-Ar, $^{40}$Ar/$^{39}$Ar, and Rb-Sr geochronological methods directly on apophyllite crystals from Kirkpatrick Basalt, the timing of low temperature hydrothermal or hydrological secondary apophyllite mineralization is significantly younger (early to middle Cretaceous ages of 95–135 and 96–130 Ma) than the primary crystallization age of $\sim$176 Ma (Fleming et al., 1999; Molzahn et al., 1999). A heating phase causing further hydrothermal alteration in the Kirkpatrick Basalt may have occurred throughout what is now exposed as the Transantarctic Mountains, much later than the initial eruptive phase likely related to rifting during the breakup of Gondwana (Elliot et al., 1999; Molzahn et al., 1999).

5.2.2. Lithium and Boron Concentrations and Fluid Tracers

One important aspect of identifying biosignatures involves identifying habitable conditions. Therefore, the concept of “follow the water” is crucial. The presence of life as we know it on Earth is closely tied to the presence of fluids, therefore textural and geochemical observations consistent with fluid-rock interactions are important. Boron and Li are two trace elements that can be highly fluid-mobile during basalt weathering/hydrothermal alteration processes (see Humphris & Thompson, 1978). Therefore, observations of B and Li distributions can serve as fluid and habitability tracers. In aqueous environments (e.g., during low temperature basalt diagenesis) B can be fixed by substitution for Si$^{4+}$ or Al$^{3+}$ into tetrahedral sites in clay lattices (Fleet, 1965; Harder, 1970; Spivack et al., 1987) or adsorbed onto surface sites in the expandable interlayer region of smectites such as those associated with Mg(OH)$_2$ especially at low temperatures (Harder, 1970; Rhoades et al., 1970; You et al., 1996). Due to a similar size and ionic charge, Li can be fixed primarily by substitution for Mg$^{2+}$ in octahedral sites in the phyllosilicate framework but can also be adsorbed within the interlayer sites. Common interlayer species such as K$^+$ or Na$^+$ have more similar charge and size to Li than B so Li is also typically preferred within the interlayers sites (Williams & Hervig, 2005). This is consistent with observations of higher Li contents compared to B in all secondary clays (Figure 5 and Figure S5 in Supporting Information S1).

The B concentrations of the secondary smectites and zeolites were likely controlled by the composition of the surface waters. Natural Iceland surface and groundwater have B concentrations in the range of 0.001–10 ppm that have been attributed to the relatively low B concentrations (0.1–6.6 ppm) in fresh tholeiitic, transitional, and alkaline basalt rocks found throughout the region (Arnórsson & Andrésdóttir, 1995). Other whole rock basalts from the Reykjanes peninsula in southwest Iceland have reported B contents of 2.4–12.4 ppm (Raffone et al., 2008), which closely agree with those of altered whole-rock Iceland hyaloclastites in this study ranging from 3.1 to 12.6 ppm (average 8.04) and fall above the average concentration of fresh tholeiitic basalts (1.2 ppm; Arnórsson & Andrésdóttir, 1995). These values also agree with the B contents of Iceland basaltic glass in this study (see Figure 5 and Figure S5 in Supporting Information S1). The two Oregon hyaloclastite tuffs (FR-12-97E and FR-12-107) also have whole-rock B concentrations near the average of the Iceland samples (8.5–9.2 ppm). The B contents of Antarctic basaltic andesite glasses have comparably low B contents. The locations in which B is concentrated are mainly authigenic phases (palagonite, phyllosilicate coatings/cements) showing a clear mineral phase partitioning. The Li concentrations of secondary phases though, less closely agree with Li concentrations generally found in surface waters of Iceland and are likely more influenced by the Li contents of glass. Hellisheiði and several other locations in Iceland have surface geothermal water Li concentrations of 0.001–0.38 and 0.05–1.2 ppm for temperatures of 50°C–100°C and 15°C–35°C, respectively (Alfredsson et al., 2013; Kaasalainen & Stefánsson, 2012). Raffone et al. (2008) reported Li concentrations of 1.8–5.7 ppm for whole-rock Iceland basalts from the Reykjanes peninsula similar to unaltered tholeiitic basalts such as from the fresh mid-Atlantic ridge
with N being bound within secondary smectites and zeolites. These minerals most likely house N as NH₄⁺ and 
used in this study. Also, it is the most altered of all the Iceland and Oregon tuffs. This observation is consistent 
(Figures 6f–6h). If Rb, Cs, and N (as NH₄⁺) are potentially exchanging/replacing K in zeolites and phyllosilicates 
N concentrations. The same samples have higher Rb/K, Cs/K, and N/K ratios than the less altered Iceland samples 
The more altered Antarctic samples with higher concentrations of K, Rb, and Cs (Figures 6c–6e) also have higher 
consider the phases in which N could reside. In fresh mafic igneous rocks, any N would likely be held in primary 
K-bearing minerals such as feldspars (Stevenson, 1959), or trapped within vesicles from degassing but concentrations in fresh basaltic glasses are less than 2.8 ppm (average 1.1 ppm, see Busigny, Ader, & Cartigny, 2005; Marty et al., 1995; Sakai et al., 1984). The overall higher N contents of the Antarctic breccias compared to the 
Iceland-Oregon tuffs (Figure 6a) generally positively correlate with the greater proportion of and difference in authigenic minerals/alteration present (Figures 3a–3c, 3g–3i and 6b), the latter mainly zeolites (heulandite-clinoptilolite vs. chabazite/thomsonite, respectively), as well as smectites (nontronite-saponite and montmorillonite). Of the younger basaltic tuffs two of the highest N concentrations (70.7 and 107 ppm) from subaerial lacustrine samples FR-12-97E and FR-12-107, respectively, from Oregon. Both samples contain abundant secondary phases comprised of amorphous gel-palagonite, proto-crystalline (fibro)palagonite (Stroncik & Schmincke, 2002), Fe-Mg smectite coatings (nontronite), and zeolites (chabazite) and calcite cements (see Nikitczuk et al. (2016), for in-depth investigation of tuffs that include FR-12-97E; see Nikitczuk (2015) for descriptions of FR-12-107). Sample FR-12-107, which is more crystallized and contains a greater proportion of secondary phases, also has the higher N concentration of the Oregon samples and the most positive δ¹⁵Ν (+7.3‰) of all the samples measured in this study. Also, it is the most altered of all the Iceland and Oregon tuffs. This observation is consistent with N being bound within secondary smectites and zeolites. These minerals most likely house N as NH₄⁺ and potentially as molecular N₂ particularly considering the porous open framework lattice structures of zeolites and their cation exchange capacities. Such N species are freely exchangeable from infiltrating solutions and can also result in fixation through substitution with cations such as K⁺ (Garrels & Christ, 1965; Stevenson, 1959, 1962; Williams & Ferrell, 1991). Additionally, NH₄⁺ and other light stable elements Li and B that are mobilized in hydrothermal fluids, can be incorporated into the same authigenic phases that form during basalt alteration by occupying various sites throughout the layered silicate framework. All three of these species can be adsorbed onto mixed-layered clays, whereas NH₄⁺ and Li and B can also be fixed by substitution for K⁺, Rb⁺, or Cs⁺ in interlayers, within octahedral sites, and within tetrahedral sites, respectively (Bobos & Williams, 2017; Williams & Hervig, 2006; Williams et al., 2001). Possible N sources (as N₂, NH₄, NO₂, and NO₃) in fluids involved in alteration are degassing from uprising magmas, meteoric surface waters, or leaching from soils or sediments/sedimentary rocks.

The more altered Antarctic samples with higher concentrations of K, Rb, and Cs (Figures 6c–6e) also have higher N concentrations. The same samples have higher Rb/K, Cs/K, and N/K ratios than the less altered Iceland samples (Figures 6f–6h). If Rb, Cs, and N (as NH₄⁺) are potentially exchanging/replacing K in zeolites and phyllosilicates formed during alteration, then higher Rb/K, Cs/K, and N/K ratios are consistent with the expected relative decrease in K or increase in Rb, Cs, and N that would be expected. Barium and Sr concentrations are very strongly correlated reflecting fractional crystallization, but the more altered Antarctic samples contain lower Ba/Rb and higher Rb/Sr ratios (Figures 6c–6m). This observation is also consistent with increasing Rb concentrations during alteration related to mineralization of phyllosilicates and zeolites and decreases in Ba and Sr possibly related to feldspar decomposition. Overall, phases shown to have concentrated Li and B (Figures 5b and 5d), and correlations of N,
K₂O, and other incompatible LILE (Figures 6c–6m) cations common to the lattice structures of authigenic phyllosilicates and tectosilicates in hyaloclastites that have the capacity to exchange them, in addition to elevated whole-rock concentrations relative to those typical of fresh basalts, are consistent with incorporation of secondary N mainly into smectites and zeolites during fluid rock interactions. On Figure 6a, the alteration rinds and zeolite cements also cluster around their corresponding whole-rock compositions, indicating that the N concentrations and δ¹⁵N values are primarily recorded in the secondary phases that comprise these components.

Most Iceland and Oregon hyaloclastites have δ¹⁵N values higher than those of MORB (−5 ± 2‰; Cartigny & Marty, 2013). However, most of these are also within the range for OIB glasses (−3.2‰ to +6.7‰; Marty & Dauphas, 2003; Marty & Humbert, 1997; Marty & Zimmermann, 1999). For fresh subglacial basaltic glasses from the neovolcanic zones of Iceland, Halldórsson et al. (2016) reported N₂ abundances of 3 ppb to 0.1 ppm (2.6–83.2 μcm³ STP/g) and δ¹⁵N values of −2.91‰ to +11.96‰. The N sampled from those glasses was obtained by in vacuo crushing and assumed to primarily represent gases released from vesicles. The samples for this study were not crushed in vacuo and most of the N contained within vesicles is presumed to have been released during crushing. Here, the pre-heating step during evacuation of sample tubes also presumably removed any later adsorbed atmospheric N₂. More than half of the fresh glasses analyzed by Halldórsson et al. (2016) were identified as having un-modified Iceland-mantle-like δ¹⁵N values (Figure 6a) between −2.3‰ and +5.7‰ (based on ⁴⁰Ar/³⁶Ar and ⁴He/⁴⁰Ar ratios). Nearly all those samples are also within the range of N concentrations and isotope compositions of OIBs and reflect thorough mixing of a heterogeneous mantle plume that includes some recycled crustal components.

Although the δ¹⁵N of many Iceland and Oregon samples from this study are within the ranges for MORB or OIB, they are appreciably enriched in N relative to these unaltered igneous lithologies (see Figure 6a). The δ¹⁵N values for the Iceland hyaloclastite samples overlap with those for fresh Iceland glass and it is possible that this similarity reflects enrichment in the glasses by interaction with N released by degassing at greater depths in the igneous section (see Bebout et al., 2018, for a similar interpretation for some seafloor-altered glasses from the Stonyford Volcanics, California, USA). Some of the more positive δ¹⁵N values compared to MORB, along with the N enrichments compared to both MORB or OIB could reflect that of contributions from organic matter in spatially associated sediments or soils (0‰–10‰; see Sweeney et al., 1978; Holloway & Dahlgren, 2002; −2 to +8; Cartigny & Marty, 2013). Sedimentary organic matter decomposition results in the release of ammonium into surrounding fluids (Boyd, 2001; Lilley et al., 1993; Macko & Estep, 1984; Papineau et al., 2005; Williams et al., 1989). In non-glacial lake sediment cores from southern Iceland (Vestra Gíslholtsvatn), δ¹⁵N values over an ~10 ka period in the same lake range from +0.5‰ to 3.5‰ (Blair et al., 2015). In Iceland precipitation the average concentration of N is 120 μg/L (Gíslason et al., 1996). The highest concentrations of dissolved inorganic N (DIN) in Iceland rivers are observed in the volcanic rift zones, particularly those linked to drainage basins of central volcanoes (Oskarsdóttir et al., 2011). Low temperature (2°C–125°C) geothermal waters of Iceland contain N as NH₄, NO₂, and NO₃ whereas high temperature areas such as where sample REY2 was obtained are dominated by N₂ (Ásgeirsdóttir, 2016) which may partly explain the MORB-like value of the LAU1-REY2 samples. These two samples with MORB-like δ¹⁵N and N concentrations are presumably less influenced by surface/near-surface sedimentary/organic sources (see Bebout et al., 2018, for a similar interpretation for seafloor-altered glasses). Large variation in the N concentrations and δ¹⁵N of the hyaloclastites could thus reflect differing degrees of alteration, fluid temperatures, local redox and pH conditions, and sedimentary and meteoric source contributions. More detailed investigation of the various sedimentary and hydrothermal components at individual modern localities (e.g., for the neo-volcanic hyaloclastites in Iceland, and perhaps also in Hawaii; see Hay & Iijima, 1968; M. R. Fisk et al., 2003; Walton et al., 2005) could elucidate the source(s) of these N alteration signatures.

The more strongly negative δ¹⁵N values for the Antarctic hyaloclastite whole-rock and separates (overall range of −20.8‰ to −7.1‰; Figure 6a) are particularly intriguing and warrant some discussion. These values could partly reflect a primary magmatic N source. The emplacement of the Dufek intrusion is based on U-Pb zircon and hornblende Ar⁴⁰Ar/³⁹Ar ages (183.9 ± 0.3 Ma), correlative and contemporaneous with other Ferrar Group rocks (i.e., Antarctic hyaloclastites in this study) and likely acted as a conduit for the magmas that were supplied to the widespread lava flows and sills (Minor & Mukasa, 1997). The intrusion was likely still hot around 179 ± 2 Ma, which is the determined age of a silicic dike in the Dufek intrusion, and was possibly cooling at a rate of 100°C/yr (Minor & Mukasa, 1997). Given that these rocks are in a higher stratigraphic position (Elliot et al., 1999), DIN as
NH₃ or N₂ degassed from the cooling/crystallizing rocks and ascending magmas could have potentially migrated upward and interacted with the Antarctic samples in this study after emplacement during subsequent hydrothermal alteration. In the absence of sediments containing organic matter, only this magmatic DIN would have been available. However, the fractionation associated with degassing would likely be a negative shift of only 1‰–2‰ (Cartigny et al., 2001), seemingly insufficient to explain the low δ¹⁵N, assuming initial MORB-like values. However, if the source was already ¹⁵N-depleted, then the reduction of N₂ could potentially result in very negative δ¹⁵N values. Negative δ¹⁵N values (−11.6‰ to −10.2‰) comparable to some of the Antarctic samples in this study (−14.3‰ to −11.5‰) have previously been observed in altered oceanic crust (AOC) DSDP/ODP drillings, some of which are minimally altered or brecciated with celadonite or calcite cements (L. Li et al., 2007). Those ¹⁵N-depleted AOC basalts, however, have very low N concentrations (2.5–3.6 ppm) in contrast to the samples in this study (51.7–1,143 ppm N). Such negative δ¹⁵N values in AOC samples were proposed to have resulted from the assimilation of NH₄⁺/NH₃ evolved from a ¹⁵N-depleted reduced mantle-like N₂ source. This could partly explain the negative δ¹⁵N values observed here, but the large enrichment in N suggests another contribution, perhaps sedimentary/organic.

Potential sources of organic N can be found in various coal measures and sediments throughout Antarctica. Widespread sedimentation occurred during the early Permian to Jurassic history of this region. At Carapace Nunatak, Ballance and Watters (1971) noted the presence of coal fragments within the Mawson Diamicite lens stratigraphically above the hyaloclastites in the Kirkpatrick basalt and in fine conglomerates in the Carapace Sandstone below the Kirkpatrick basalt that were likely eroded from Beacon Group rocks. The Carapace Sandstone contains numerous mudstone clasts, conceivably organic- and thus N-rich. The N concentration and δ¹⁵N values. Negative δ¹⁵N values (−11.6‰ to −26.2‰) have been measured in mineral nitrate from flows directly overlie coal-bearing Beacon sandstones and shales of Permian age (Barrett, 1968; Grindley, 1963). Some locations such as at the Beardmore Glacier area in the Transantarctic Mountains, Kirkpatrick Basalt Sandstone below the Kirkpatrick basalt that were likely eroded from Beacon Group rocks. The Carapace Sandstone contains numerous mudstone clasts, conceivably organic- and thus N-rich. The N concentration and δ¹⁵N values. Negative δ¹⁵N values (−11.6‰ to −26.2‰) have been measured in mineral nitrate from flows directly overlie coal-bearing Beacon sandstones and shales of Permian age (Barrett, 1968; Grindley, 1963).

Interestingly, modern Antarctic soils from Wright Valley, Victoria Land, Antarctica have δ¹⁵N values of −11.5‰ to −23.4‰, with one of the lowest δ¹⁵N values ever reported for terrestrial samples (−49‰) measured from an algae collected from a small saline pond near the Wright Upper Glacier (Wada et al., 1981). These extremely low δ¹⁵N values are explained by isotopic fractionation at high nitrate concentrations and low light intensities that accompanied assimilation of ¹⁵N-depleted NO₃⁻ derived from atmospheric precipitation, a major source of nitrate for Antarctic soils. Likewise, low δ¹⁵N values (−9.5‰ to −26.2‰) have been measured in mineral nitrate from soils of McMurdo Dry Valleys, Victoria Land, Antarctica (Michalski et al., 2005). Those authors suggested that the significant δ¹⁵N depletions may be related to the mixing of different atmospheric NO₃⁻ sources. It is unknown whether the Permian to Jurassic sediments associated with the alteration of the Antarctic hyaloclastites had similarly low δ¹⁵N values. If so, the data presented in this paper for the Antarctic hyaloclastites could reflect transfer of this N by circulating hydrothermal fluids to produce the δ¹⁵N reported in this paper (cf. Stüeken, Boocock, et al., 2021; Stüeken, Gregory, et al., 2021).

5.4. The Possible Role of Microbes in Alteration Processes

Numerous observations of natural glassy volcanics and experiments using natural or synthetic basalts indicate that such materials are habitable to microbes and that microbial communities can play an important role in
the alteration process. Bacteria have been identified in association with altered parts of subaerially produced palagonite (Thorseth et al., 1992, 1995, 2001), glassy pillow lava rims of ocean basalts (Furnes et al., 1996; Torsvik et al., 1998) and sub-glacial hyaloclastites of Iceland (Cockell, Olsson, et al., 2009). Thorseth et al. (1995) inoculated natural basaltic glass samples immersed in growth media with bacteria derived from Surtsey tuffs and observed that microbes have an affinity to colonize glass surfaces and can also chemically etch or bio-erode surfaces producing pits. Similarly, experiments exposing nuclear waste glass to seawater and marine cyanobacteria show that greater glass corrosion occurs in the presence of microbes (Staudigel et al., 1995). In batch bacterial colonization laboratory experiments using ICPD HSDP2 basalts and synthetic basaltic glasses, Stranghoener et al. (2018) found that Fe dissolution may be initiated by microbial activity and that bacteria more favorably form biofilms on basaltic glasses with residual stress and high Fe(II) contents. The oxidation of structural Fe(II) (e.g., Shelobolina et al., 2003) and reduction of Fe(III) (e.g., Liu et al., 2011; M. E. Bishop et al., 2011) in clay minerals by various bacteria and/or archaea is a well-documented occurrence. Microbial surfaces can also act as authigenic phyllosilicate nucleation and growth sites (Konhauser & Urrutia, 1999). Colonization modules deployed in hydrothermal deep-sea sediments of the Guaymas Basin indicate a large microbial diversity in oceanic basalt colonizers and that secondary barite and pyrite mineral formation may be microbiologically mediated (Callac et al., 2013). Rather than being regarded as a purely physicochemical process, the alteration of basaltic glass and thus the formation of secondary phases, chemical exchange that occurs during basalt alteration and the global cycling of elements is believed to be significantly affected by microbial bio-catalyzation.

5.4.1. Putative Microbial Traces in Altered Glasses

Petrographic examination of Iceland (LAU1, REY2) and Antarctic (KBH17, CPN2) thin sections have revealed various textural features (Figures 3d, 3e, 3k and 3l and Figure S1 in Supporting Information S1) comparable to the widely documented variety of tubular and granular forms observed propagating into fresh basaltic glass from palagonitic alteration fronts thought to be the result of microbial activity (Banerjee & Muehlenbachs, 2003; Benzerara et al., 2007; Cockell, Olsson-Francis, et al., 2009; Cousins et al., 2009; Furnes & Staudigel, 1999; Furnes et al., 1996, 2001a, 2005, 2007; M. Fisk & McLoughlin, 2013; M. R. Fisk et al., 1998, 2003; Nikitczuk et al., 2016; Thorseth et al., 1995, 2003; Torsvik et al., 1998; Walton, 2008). Several forms as described by (M. Fisk & McLoughlin, 2013) are observed here, including, simple, branched, mossy, network, palmate, or crowned varieties. McLoughlin et al. (2007) proposed a set of criteria for establishing the biogenicity of putative microbial textures that include establishing a primary geological context, biogenic morphology and behavior, and geochemical evidence for biological processing. Tubular textures are associated with locations that either acted as fluid conduits or were in contact with younger fluids such as clast margins, vesicles and fractures. When propagating from fractures, they are distributed asymmetrically, and usually lack a smooth isopachous palagonitic alteration front. However, where tunnels exist along fractures in Antarctic samples, they appear to be later fractures surrounded by fresh glass with no palagonite or clay-zeolite replacement. In LAU1 and REY2, the presence along vesicle surfaces or clast margins that are coated in phyllosilicates and/or zeolite or carbonate cemented (Figures 3g, 3h, 3j and 3l) indicates that they were formed prior to coating and cementation placing them within the diagenetic context. Tubules preserved in palagonite glass (Figure S1e in Supporting Information S1) and crosscut by later fractures also indicate formation prior to palagonitization and later fractures. KBH17 and CPN2 tubular textures are more closely associated with alteration fronts but scattered and in many cases obscured within the complex clay-zeolitic replacement and probably abiotic clay-filled dissolution channels. KBH17 and CPN2 contain elongate channel-like features, completely infilled with smectites of slightly differing composition than exterior coatings (e.g., more Ti-enriched) with irregular boundaries and shapes, and variable diameters (10–20 μm) than the typical microbes found in similar rock types. In close association with these features, however, are 1–3 μm circular cross-sections of tunnels at the section surface. Rarely observed are preserved tunnels within alteration zones that have been completely replaced by phyllosilicates, an observation indicating their formation prior to glass alteration. The Antarctic samples thus may have multiple generations of tubular textures. No tubules contain longitudinal striae, mineral grains, or angular cross sections (oblong to circular) or clear intersections with other tubules. Furthermore, they typically have preferred orientations (many propagating in similar directions and usually perpendicular with respect to glass surface), sometimes directed toward Fe-bearing primary minerals or around small fractures, and forms that include terminal enlargements/crowns, annulations and diameters in the range of microbial sizes (generally 1–5 μm). Therefore, abiotic ambient inclusion trails (see Wacey et al., 2008) are confidently ruled out.
Geochemical evidence of bioprocessing associated with putative microbial textures is more ambiguous and variable. The interiors of tubular-granular alteration zones of LAU1 and REY2 show depletions in Ca, Al, Mg, Na, and Li, enrichments in Ti and B, and variable Fe, K, P, and Ni (enrichments, depletions, and approximately equal) with respect to fresh glass and do not appear to be infilled with identifiable clays, but Fe is more commonly enriched. Enrichments in Ti may contribute to preservation of tubular/granular features as suggested by titanite mineralization of morphologically similar textures in ancient meta-basalts (Banerjee et al., 2007; Izawa, Banerjee, et al., 2019). Boron has long been recognized as a micronutrient in plants (Swanback, 1927; Warrington, 1923) but more recently has also been established as an essential growth requirement for certain types of bacteria such as cyanobacteria (Bonilla et al., 1990), and as an important nutrient for yeasts (Bennet et al., 1999) and animals (Nielsen, 2002). The observation of tubular alteration textures with B enrichments in the interior in the absence of infilling clays (Figure S5 in Supporting Information S1) may be linked to microbial remnants, although this requires more in-depth investigation.

Phosphorus is a biologically important element to consider as it is a common limiting nutrient. Slight enrichments in P within tubular and granular alteration zones could be associated with preserved organics, however, more obvious is its incorporation into coarser-grained secondary apatite. Morphological observations suggest apatite formation was possibly microbially mediated. Radial 5–10 μm mineralizations are embedded within smectite coatings that are rounded nearest to the smectite-glass interface and inter-grown and splayed away from the smectite-glass interface. SEM imaging reveals that the rounded boundaries of some of the latter forms appear to display either mid-boundary semi-septate divisions creating the appearance of a pair of lobes or two adjacent 2–3 μm round to oblong objects with porous 1–2 μm cores as if mineralization was initiated about the surfaces of the pair of rounded cell-sized bodies (Figure 3j). The very low whole-rock P2O5 wt. % of LAU1 and REY2 (0.2 and 0.24, respectively) and the WDS/EDS of fresh glasses range (0–0.24 wt. %), and the lack of minor primary apatite, suggest that unaltered components in the basalts do not represent a significant source of P. Dissolved P released from organic matter by bacteria, however, may be locally partially exchanged and incorporated into authigenically precipitated phosphate minerals (Blake et al., 1998). Secondary apatite inclusions within smectite have previously been reported in altered glassy basalts (e.g., Walton & Schiffman, 2003), although not as clear radial structures. Comparable 3–9 μm radial apatite structures interpreted as microbially mediated P mineralization, however, have been reported in various banded iron formations, cherts, shales, and phosphorites (e.g., S. Sun et al., 2014; Y. L. Li et al., 2013). Microbially mediated apatite has also been produced in laboratory experiments (e.g., Blake et al., 1997) with ovoid structures (Hirschler et al., 1990; Lucas & Prévôt, 1985) and radial forms (Blake et al., 1998) supporting the potential microbial origin of similar features observed in natural samples. The possible microbial origin of the apatite here is based more on morphology though and it is acknowledged that abiotic reactions are capable of producing similar textural features, notably ovoid or coccolid forms (Blake et al., 1998). Further investigation targeting DNA and organic C contents may support their microbial origin.

5.5. Implications for Astrobiology: The Suitability of Volcaniclastic Materials as Targets for Mars Sample-Return

Basalts are widespread across the Mars surface and an amorphous material that may consist of volcanic or impact generated glass, and mineral assemblages indicative of aqueous or low temperature alteration of basalts have also been identified (Head & Wilson, 2007; Jaeger et al., 2007; J. F. Mustard et al., 2008; McSween et al., 2010; Squyres et al., 2007). The chemical composition and assemblage of secondary phases in hydrothermal or low-temperature altered volcanic or impact generated glasses reflect the characteristics of the environment including temperature, pH, redox conditions, water-rock ratio, surface area, porosity and altering fluid and primary glass composition. Despite the meta-stability of glass, volcanic or impact generated, and hyaloclastites and related materials could remain intact for billion-year timescales through burial protection from surface weathering conditions (Cannon & Mustard, 2015). Recently exhumed materials may now be present at or near the surface and readily accessible for sampling which could contain considerable information regarding abiotic surface or biogeochemical processes at the time of formation.

The successful detection of a biosignature in a Martian sample would necessarily have to include a combination of micro-scale physical, biomolecular and metabolic lines of evidence (J. Mustard et al., 2013). We refer to a sequence of analyses proposed by Kmínek et al. (2014), and similar to our approach, for detecting biosignatures in a solid return sample that has reached the point of being removed from the sample collection container.
The overall workflow would proceed with non-destructive, non-invasive analyses such as imaging, tomography, and spectroscopy, followed by progressively more invasive and ultimately destructive techniques requiring more specific sample preparation (e.g., electron microscopy, and mass spectrometry). This would involve the integration of multiple microanalytical methods that can, together, deliver a finely resolved spatial and chemical framework linking microstructures, authigenic minerals, elemental/molecular components and their distributions, and the processes that produced them under particular environmental conditions.

The range of independent observations that would be required to identify a collective biosignature might include visible textures, biological remnants such as filamentous structures and organic remains (especially in association with biogenic textures), biochemical markers such as DNA/RNA, spatially concentrated biologically important elements such as N and C (and S or P), and stable isotope patterns such as δ¹³C and δ¹⁵N in secondary phases indicative of biological fractionation (e.g., Furnes et al., 2002). The physical traces of paleo rock-hosted life in the form of tubular or granular endolithic microborings may be present in volcanic substrates as evidenced in submarine, subglacial and continental lacustrine pillow basalts and hyaloclastite breccias and tuffs (Banerjee & Muehlenbachs, 2003; Benzerara et al., 2007; Cockell, Olsson-Francis, et al., 2009; Cousins et al., 2009; M. Fisk & McLoughlin, 2013; M. R. Fisk et al., 1998, 2003; Furnes & Staudigel, 1999; Furnes et al., 1996, 2001a, 2005, 2007; Nikitczuk et al., 2016; Thorseth et al., 1995, 2003; Torsvik et al., 1998; Walton, 2008) and could also potentially be found in meteorite impactite glasses (Sapers et al., 2014). Palagonitization may also result in microbial cell encrustations leaving bacteriomorph-like structures in altered basalts (McLoughlin et al., 2011). In addition, a range of geochemical tracers that may represent remnants of biological material or records of metabolic processes of microbes could potentially be detected. These may include microbial DNA or RNA associated with bio-alteration textures (Giovannoni et al., 1996; Thorseth et al., 2001; Torsvik et al., 1998), re-distributions of biologically important elements, nutrients and trace metals at the micro-to-nanoscale, including co-locations of C, S, N, and P possibly representing cellular remains, K concentrations within tubules or granular palagonite zones (Torsvik et al., 1998) or micropores in glass alteration phases (McLoughlin et al., 2011), depletions in Fe, Mg Ca, Na, Co, Ni Cu, and Zn, within rock matrices associated with microbial textures (Alt & Mata, 2000; Benzerara et al., 2011) or C:N and N:P ratios indicative of microorganisms (Fagerbakke et al., 1996; Goldman et al., 1987; Redfield et al., 1963). Bio-molecular remnants such as protein-rich organic compounds may be found associated with putative microbial textures (Izawa, Dynes, et al., 2019). Stable isotopes also provide a powerful geochemical tracer for bioprocessing and establishment of conditions tolerable to microbes. Carbon isotope fractionation patterns (enrichments in ¹²C relative to fresh crystalline samples) associated with the preference for ¹²C over ¹³C during oxidation of organic material, that produces isotopically light CO₂, may be recorded in disseminated carbonates (Furnes & Staudigel, 1999; Furnes, Muehlenbachs, et al., 2001, 2004, 2005; Torsvik et al., 1998). Likewise, N enrichments and isotope fractionations (¹⁵N-enriched) related to biogeochemical cycling may be preserved in alteration assemblages that include various silicates identified on the Mars surface (Bebout et al., 2018; Buseigny, Laverne, & Bonifacie, 2005; Hall, 1989; L. Li et al., 2007). Although the detection of organic molecules and associated stable isotope patterns are a major target on Mars, it is noted that ionizing cosmic radiation can significantly degrade organic molecules (Pavlov et al., 2012) and in some instances could result in changes to primary biologically produced stable isotope ratios effectively offsetting preservation processes (Hays et al., 2017). Oxygen isotopes of carbonates, which commonly form during basalt alteration, could potentially be used as paleo-thermometer to establish alteration temperatures (Kim & O’Neil, 1997; McCrea, 1950) and indicating whether such thermal conditions are within the tolerable range for known organisms on Earth. Combined use of the δ¹⁸O, δD, and ⁶⁰Sr/⁶⁰Sr of secondary carbonates and silicates in altered glassy volcanioclastics from Antarctica has made it possible to distinguish source water compositions and temperature constraints has been demonstrated (e.g., Antibus et al., 2014). Isotope systematics of metabolically important transition metals such as Ni could also provide biomarkers (Cameron et al., 2009) and multivalent transition metals (e.g., Fe, Cr, and Mo) are also indicative of redox conditions (see Figure S3 in Supporting Information S1 and related discussion). Conversely, consideration of non-redox-sensitive trace element compositions such as Li and B and their isotope compositions may be useful in tracing the existence of associated organic matter (e.g., Williams et al., 2015).

5.5.1. Other Information Attainable From Study of Mars Volcanic Glass

The presence of primary igneous materials such as unaltered glass, igneous minerals, primary silicate melt or phenocryst inclusions, or rare gasses trapped within vesicles during magma degassing in any return sample presents the prospect of obtaining a host of other information that represent pristine samples of mantle-derived magmas and their volatile contents (see Schiano, 2003 and references therein) and differentiation processes such
as assimilation and fractional crystallization. Such information would also contribute to reaching Mars sample-return science goals. K-bearing igneous minerals such as feldspar phenocrysts and radiometric geochronological methods such as the ⁴⁰Ar/³⁹Ar technique or K/Ar dating could be used to determine crystallization ages (Eberhardt et al., 1971; Turner, 1970). Isotope systematics of Rb-Sr, Sm-Nd, or Re-Os of primary mineral separates (e.g., pyroxene and olivine) or internal mineral-bulk rock with mixing and assimilation-fractional crystallization modeling have been applied to Martian meteorites to gain insight into petrogenetic controls and Martian mantle chemical evolution (e.g., Borg et al., 2002; Brandon et al., 2012). Variations in δ¹⁵N values and abundances of N₂, radiogenic ⁴⁰Ar and primordial ³⁶Ar, ¹³C and ¹²C (N/³⁶Ar, N/³⁶Ar, ⁴⁰Ar/³⁶Ar, ¹³C/³⁶Ar, ¹²C/³⁶Ar, N/¹³C, and N/¹²C ratios) within gas inclusions compared to atmospheric values (Mahaffy et al., 2013; Nier & McElroy, 1976; Owen et al., 1977; Wong et al., 2013), could lead to estimates of Martian mantle endmember compositions (e.g., Halldórsson et al., 2016; Marty et al., 1995). Conversely, gases trapped within inclusions of impact generated glasses may potentially provide preserved samples of the earlier Martian atmosphere. Nitrogen and noble gas (Ar, Kr, and Xe) elemental and isotopic compositions within glass inclusions in Martian meteorites such as the shergottites (e.g., EETA 79001) indicate that samples of the Martian atmosphere can become trapped during impact shock processes (e.g., Becker & Pepin, 1984). Any sampling of the early atmosphere or primitive mantle could represent a reservoir that can act as reference standard for measuring Mars isotopes such as N. Additionally, syngenetic indigenous N in Noachian-age phyllosilicates could be a possible abiological surface reservoir that can be characterized and used as a reference standard for N isotopes on the Mars surface (van Zuilen, 2008).

6. Conclusions

The textures, mineralogy and major and trace element and N geochemistry of terrestrial (non-marine) ancient (Jurassic) Antarctic basaltic andesitic and modern (Pliocene-Pleistocene) subglacial and continental lacustrine Iceland and Oregon basaltic hyaloclastites, respectively, were investigated using a combination of in situ micro-imaging and chemical methods and non-in situ mass spectrometry. Comparison of older and more crystalline Antarctic breccias and younger less crystalline (containing palagonite) Iceland and Oregon hyaloclastites, and textural-chemical features, allow consideration of deposit age and alteration stage and the control of evolving fluid composition and pH on the formation of secondary assemblages, respectively. More advanced alteration in Antarctic breccias, compared to the modern Iceland tuffs, is consistent with greater enrichments in LILE relative to concentrations in fresh MORB. Major secondary minerals consist of saponite-nontronite and montmorillonite paragenetically followed by chabazite or thomsonite and calcite in Iceland samples, whereas nontronite-saponite are followed by heulandite-clinoptilolite and calcite, variably fluorapophyllite, erionite, quartz and later fluorapophyllite in Antarctic hyaloclastites. Mineral assemblages and compositions and geological information indicate circum-neutral meteoric source waters and mostly open system, increasingly alkaline low-temperature alteration conditions of ~60°C–100°C (Iceland) and ~60°C–170°C (Antarctica), encompassing the range of temperatures tolerable to life. The distributions and concentrations of the fluid mobile trace elements Li and B provide further evidence for significant fluid interactions and in turn habitable alteration conditions. All samples contain putative microbial traces as granular and tubular glass alteration textures within a primary geological (diagenetic) context and bio-morphologies and/or indications of behavior observed in other ancient or modern submarine, subglacial and subaerial hyaloclastites. Possible microbially mediated apatite is also observed. Basaltic andesites show evidence of at least two generations of alteration.

All whole-rock hyaloclastites, alteration rinds and cement phase separates contain measurable quantities of N mostly higher than those in fresh MORB or OIB and reflecting significant enrichment beyond that attributable to igneous processes alone. More positive δ¹⁵N values and N enrichments relative to MORB or OIB could reflect NH₄⁺ released into fluids from the decomposition of organics in local sediments/soils. Other MORB/OIB-like compositions may reflect N degassed from magmas at greater depths and conveyed into fluids that interacted with glasses. Antarctic samples are considerably more enriched in N (51.7–1,143 ppm) and have more negative δ¹⁵N values (~20.8‰ to ~7.1‰) than the Iceland and Oregon basaltic tuffs (the latter containing 1.6–172 ppm N with δ¹⁵N of ~6.7‰ to ~7.3‰). Such negative δ¹⁵N values may partially reflect assimilation of NH₄⁺ from a δ¹⁵N-depleted reduced mantle-like N₂ source. However, given the nearby sedimentary organic reservoirs (i.e., Permian coal measures, fossil and coal-bearing clastic sediments, Antarctic soils with low δ¹⁵N values) the N enrichments could reflect hydrothermal fluids interacting with NH₄⁺ mobilized from the decomposition and thermal breakdown of organic matter. Nitrogen contents generally correlate with overall degree of alteration.
deduced petrographically and by other geochemistry. A modest correlation of N with K$_2$O and stronger correlations of K$_2$O with other incompatible elements likely reflect a complicated siting of fixed secondary N as NH$_4^+$ for K$^+$ and other cations. Such complex siting, however, also likely includes organically bound NH$_4^+/\text{NH}_3$, or potentially N$_2$, most importantly in hydrated phyllosilicates and zeolites, controlled by multiple factors including differences in crystal lattice properties such as cation exchange and micro or mesopore dimensions. We suggest that more detailed investigation of the possible magmatic, sedimentary/organic, and hydrothermal contributions at individual modern localities (e.g., the neo-volcanic hyaloclastites in Iceland and Hawaii) is necessary to further elucidate the generation of these N alteration signatures.

In building toward the development of robust biosignatures, an important aspect of future work will involve the assessment of diagnostic organic molecule and organic C preservation in associated authigenic phases and textures that would add to detailing the biogeochemical context for textures and N contents and isotope compositions. It is well known that clay minerals promote the preservation of organic matter and mineral surface areas, and grain sizes can strongly correlate with organic matter concentrations (Hedges & Keil, 1995). Smectites for example, can trap organic matter, within interlayer sites through adsorption (Arnason & Keil, 2000; Hazen & Sverjensky, 2010), that may also be associated with fixed NH$_4^+$ (J. L. Bishop et al., 2002). Carbonaceous materials not adsorbed onto clay and possibly related to the generation of microbial textures may also be detectable (Wacey et al., 2014) and it has been suggested that organic matter and associated light elements from organic decomposition (e.g., Li, B) could be sequestered by and protected in clay interlayers or within zeolitic mesopores (Zimmerman et al., 2004). A future goal would be identifying direct associations of organic materials, N and C enrichments and isotopic compositions, micro-textures and authigenic phases, including amorphous and crystalline palagonite, potentially at the micro-to nano-scale using in situ methods (e.g., Lepot et al., 2013; Wacey et al., 2014; Williford et al., 2013) to complement non-in situ methods such as sealed tube combustion IR-GC-MS used in this study. This would include a more comprehensive survey aimed at determining the specific mineral phases that can incorporate and store N and potentially preserve isotopic records of biogeochemical processing on Earth and thus potentially on Mars. Using a full array of analytical methods at multiple spatial scales, a wide range of textural and chemical data, demonstrated here and in various other studies (e.g., Antibus et al., 2014; Cannon et al., 2015), can be obtained from altered hyaloclastites and used to delineate conditions of habitability, physical or chemical traces of life in addition to other igneous/planetary processes. Considering the widespread occurrence of glass-bearing volcanic or impactite deposits and commonly associated alteration minerals on Mars, hyaloclastites should be considered as viable targets for future sample-return.

**Conflict of Interest**

The authors declare no conflicts of interest relevant to this study.

**Data Availability Statement**

The in situ and whole rock and mineral separate major and trace element geochemistry and N concentrations and isotopic compositions of altered ancient Antarctic basaltic andesitic and modern subglacial and continental lacustrine basaltic hyaloclastites from Iceland and Oregon (whole rock ICP-MS/ICP-OES/PGNAA, IR-GC-MS, and in situ WDS) in this study are available at the EarthChem Library open-access repository via https://doi.org/10.26022/IEDA/112220 with Creative Commons Attribution-ShareAlike 4.0 International (CC BY-SA 4.0) licensing (Nikitczuk et al., 2022).

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