NITROGENOUS MARS-ANALOG POTASSIC AND MICRO- AND MESOPOROUS MINERALS: RELEVANT TARGETS FOR MARS SAMPLE-RETURN

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Introduction: The fundamental relationship of N with life on Earth raises the possibility that it could be equally important for extraterrestrial life elsewhere in our solar system such as on Mars and beyond. Nitrogen is necessary to form molecules such as proteins and amino and nucleic acids used in metabolic and enzymatic activity and is also converted to molecular species of various oxidation states (e.g., NH_4^+. NH_3, NO_3^-) during biogeochemical cycling. On Earth, these transformations are primarily mediated by microbes. Nitrogen mass fractions and isotope compositions of atmospheric and geologic reservoirs can therefore provide important information about the chemical evolution of planets including the potential development of biogeochemical cycling.

Nitrogen on Mars. Viking lander and Mars Science Laboratory (MSL) measurements show that Mars' atmosphere is enriched in the heavier ^{15}N isotope (with respect to Earth) and contains a significantly lower concentration of N than Earth (~2% vs. 78%) [1-3]. Nitrogen may have been lost from the Martian atmosphere to space over time through escape processes but an appreciable quantity may be sequestered by surface materials during exchange between the atmosphere and crustal components. However, little is currently understood about such processes or the phases potentially involved. It was previously hypothesized that nitrates would be a likely form of N on Mars, which are typical of very dry dessert soils on Earth, and that some ammonium (NH_4^+) could be bound to phyllosilicate minerals [4]. Evidence of fixed N in the form of nitrates has recently been found in sedimentary samples from Gale Crater by the MSL Curiosity rover [5-6]. Evidence for NH_4^+ however, has not been identified yet, but N_2 and/or NH_3 may have played a more important role in maintaining more elevated surface temperatures and atmospheric H_2O on ancient Mars [7-8]. In our search for evidence of life beyond Earth or information that could reveal the chemical evolutionary past of Mars, determining the inventory, form, distribution and storage phases of N is a critical factor for understanding the probability of life originating and evolving on another planetary body such as Mars [9-11].

A Survey of Nitrogen in Mars Surface Analog Materials: Investigations of the Mars surface have revealed a variety of hydrated minerals [12], many of which are typically associated with altered basalts. These include Fe/Mg and Al-phyllosilicates, zeolites, sulfates, siliceous deposits and carbonates. If a substantial portion of N has been stored within solid phases present at or below the surface it is expected that certain phases will be more susceptible to N incorporation than others and thus may represent more suitable targets for future investigation (e.g., Mars2020 sample return). In this framework we are performing a detailed survey of the natural N-retentivity in Mars-analog minerals (using a sealed tube combustion GC-IRMS method) [see 13] and their potential to preserve biogeochemical and/or planetary-environmental records.

Potassic and Microporous Mineral Phases. Most phyllosilicates and zeolites analyzed here were formed in diagenetic to low temperature or hydrothermal basaltic or silicic volcanic or intrusive igneous environments and occur either as direct alteration products of glass/ash or minerals or as pore-filling cements, amydules or vugs. Minerals show a large range in both N contents (from 0 to 99121.5 ppm and $\delta^{15}N_{air}$ values (from -33.0 to +12 ‰) (Fig.1). The phyllosilicates show the widest range in N content (from 16.8 to 99121.5 ppm) followed by the zeolites (0.5 to 4827 ppm), sulfates (from 59 to 3459.9 ppm) and silica, which all have similar concentrations (48.3 to 62.1 ppm, $\delta^{15}N$ = -0.4 to +3). Smectite clays (saponite, nontronite, montmorillonite) have 18.8 to 171.8 ppm N_2 and $\delta^{15}N$ values from -33 ‰ to -16.2 ‰. Out of the 44 samples, six have near atmospheric isotope values (i.e., $\delta^{15}N_{air} = 0 \pm 2$ ‰). Out 38 minerals with measurable quantities of N, 23 have $\delta^{15}N$ values similar to organic matter in sediments [0-10‰; see 14] and 29 are within the range of or are more positive than MORB "mantle values" [-5 ± 2 ‰; see 15].

Basaltic Hyaloclastites. Basalts are widespread across the Mars surface and an amorphous material that may consist of volcanic or impact generated glass as well as mineral assemblages indicative of aqueous or low temperature alteration of basalts have also been observed [16-18]. Nitrogen and additional microchemical and whole rock major and trace element geochemistry from well-characterized altered basaltic and basaltic andesitic hyaloclastites from Iceland-Oregon and

Antarctica, respectively, are used as contextualized case studies here and compared with mineral analyses. In ppm-δ^{15}N space (Fig. 1) the Iceland-Oregon basalts (1.6 – 171.9 ppm N; δ^{15}N from -5.7 to +8.2 ‰) overlap with phyllosilicates, zeolites, sulfates and amorphous silica-quartz ranges and have δ^{15}N values within the MORB-OIB range whereas most samples contain higher N contents than MORB-OIB and also overlap with other altered oceanic basalts. Confirmed authigenic minerals include saponite, montmorillonite, chabazite, thomsonite and calcite and indicate alkaline formation waters at temperatures of 60° to 100°C. Antarctic samples, however, are more enriched in N and have significantly more negative δ^{15}N values (51.7 – 1577.1 ppm N; δ^{15}N values from -19.8 to -6.1 ‰) overlapping with phyllosilicates. They are also more enriched and more negative than MORB-OIB but have a N concentration range comparable to phyllosilicates, zeolites, sulfates, and silica-quartz. Confirmed minerals include nontronite, saponite, heulandite-clinoptilolite, erionite, apophyllite, calcite and quartz and indicate alkaline conditions at temperatures of 60° to 100°C. For the Iceland-Oregon basaltic tuffs, 11 of 21 show δ^{15}N values similar to organic matter in sediments whereas the Antarctic whole rock and separates generally show more negative δ^{15}N values (-19.8 to -6.1 ‰) and moderately to significantly higher N contents than the Iceland-Oregon basalts.

Nitrogen Citing and Records of Geochemical Processes. Previous investigations of modern altered seafloor basalts, palagonitized glasses, whole rock Mesozoic ophiolites and ancient Archean terrane (Abitibi greenstone complex) have shown N enrichments and δ^{15}N values of up to 491 ppm and +9.1‰, respectively [17-20]. These enrichments and higher δ^{15}N values are attributed to the incorporation of N associated with sedimentary/organic materials during alteration by circulating hydrothermal fluids. Such nitrogen may be trapped as N_2 or structurally bound as fixed NH_4^+ replacing K^+ in secondary minerals such as phyllosilicates. Generally, Antarctic samples with higher N contents have higher concentrations of K_2O and other geochemically similar LILE cations (e.g., Rb, Cs, Ba). Based on N-C SIMS mapping, in Antarctic samples heulandite-clinoptilolite, and in Iceland samples saponite-montmorillonite, are the main phases in which N is located. These phases usually contain such cations. Typically negative δ^{15}N values in basalts are associated with magmatic degassing, but the enrichments relative to MORB of all samples are indicate sedimentary component.

Conclusions: Terrestrial phyllosilicates, zeolites, sulfates, and siliceous deposits contain measurable quantities of N. Scatter of N data plotted against LILE suggests citing multiple species including NH_4^+/NH_3, N_2 and possibly organically bound N. If Ancient Mars had a significantly more N-rich atmosphere it is possible that a significant amount of N may be stored in phases on the Mars surface in forms other than nitrates. Minerals storing ancient N may record environmental changes and potentially the development of biogeochemical cycling. Nitrogenous phases associated with altered basalts should be given consideration in selecting future Mars sample targets.

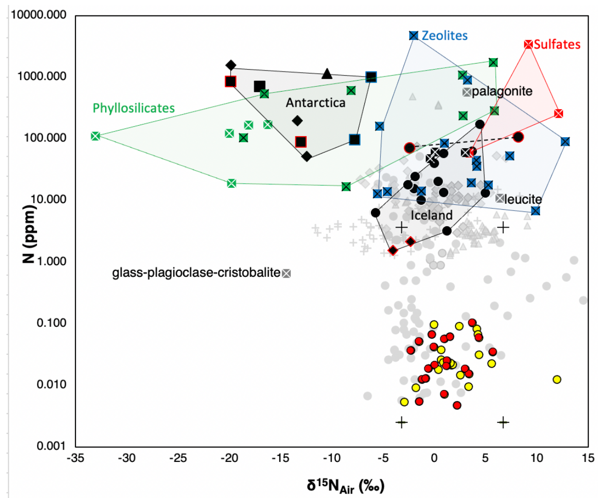

Figure 1: N concentrations and δ^{15}N values of various globally distributed Mars—analog minerals and Antarctic and Iceland-Oregon hyaloclastites. Also plotted are fresh basaltic glass [red-yellow; from Halldórsson et al., 2016) from Iceland and fresh and altered oceanic crust.

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