

FIXED NITROGEN AS A TRACER OF HABITABLE ENVIRONMENTS ON MARS: ENABLING IN-SITU SPECTRAL DETECTION. E. F. Gibbons^{1*}, R. J. Leveille¹, and K. Berlo¹, ¹Department of Earth & Planetary Sciences, 3450 University Street, Montreal, Quebec, Canada, H3A 0E8. *erin.f.gibbons@gmail.com

Introduction: Terrestrial life needs a fixed form of nitrogen (N) to craft its biomolecular structures. Fixed N is often a limiting nutrient and controls the biomass and diversity of an environment. Mapping fixed N species on Mars' surface may provide a means to assess past and present habitability constraints. Such fixed N species are predicted to be deposited globally on Mars and have been detected *in situ* as nitrates by the Sample Analysis at Mars (SAM) tool [1, 2]. However, SAM can only query small samples at infrequent intervals and a tool for regular, remote detection is needed to determine the abundance and distribution of Mars' fixed N pool.

Laser-induced breakdown spectroscopy (LIBS) can rapidly detect light elements, including N, and is a part of all three active Mars rovers. Unfortunately, little is reported on the LIBS N spectrum, likely due to detection issues. There are three major challenges in detecting LIBS N: (1) the high ionization energy results in weak emission lines, (2) the strongest lines emit at <200nm, which is below the range of most detectors, and (3) atmospheric N₂ interferes with the signal from the target [3]. Consequently, LIBS is seldom used to study N on Earth and there lacks consensus on which emission lines are best suited for detecting or quantifying N (e.g., [3, 4]). However, LIBS signals are stronger on Mars [5] and there is less N₂. We therefore present experiments designed to establish a baseline understanding of the LIBS N spectrum from Mars-relevant materials to lay the groundwork for future chemostratigraphic surveys.

Samples: The NO₃⁻ ion can be sequestered on Mars by forming salts with soil cations. To simulate this, we powdered reagent-grade nitrate salts of Mars-relevant cations: Ca(NO₃)₂, Fe(NO₃)₃, KNO₃, Mg(NO₃)₂, and NaNO₃. Then mixed the salts individually with a mineralogical Mars simulant from the Exolith Lab [6] at concentrations of 0.5, 5, 10, 15, 25, and 30 wt% of the NO₃⁻ ion. We analyzed pressed pellets of each mixture alongside pure salt and simulant samples as controls.

Methods: We used a J200 LIBS instrument with a 213 nm pulsed laser operating at a 10 Hz and a broadband 6 channel CCD spectrometer yielding a spectral window from 190-1040nm. We used He gas flow to eliminate ambient N in the sample chamber. We optimized firing conditions based on the signal-to-noise ratio of the line at 746.8nm, which has been reported as the strongest N line in our spectral range [3]. We found a 25µm spot-size, 1.52 mJ/pulse energy, and a 0.15µs gate delay gave the best signal.

We measured each sample at 5 locations to ensure a good representation of composition. Each measurement comprised 100 laser pulses organized in a line. We then normalized the summed spectra to their total intensity.

Identifying N lines: Our initial survey of N lines was based on spectra from the pure salts and guided by the following criteria: lines must (1) match a reference N line position in NIST [7], (2) be visible above background emission, (3) be sufficiently free from other element lines, and (4) be confirmed by an *absence* of the line of interest in the Mars simulant control sample.

Results: Table 1 lists the twenty-four lines we observed to meet the initial criteria. All lines are attributed to N(I) emission; no lines from ionized N were confirmed. As expected, relative to the pure salts, the N line intensities were lower in the mixtures as they have a lower mole fraction of N. We did not observe any of these N lines in the samples with 0.5wt% NO₃⁻, suggesting this is below the limit of detection (LOD) achievable by our setup. Only five N lines were detectable in the mixtures with the next lowest NO₃⁻ concentration, 5wt%. We consider these five lines, bolded in Table 1, as the most useful for detection since they yield a signal across the largest range of N contents.

To compare the utility of these five lines for future quantitative analysis, we averaged the spectra acquired from each sample into a single data file and built univariate calibration curves for each salt series by plotting the integrated area of the candidate N lines against the mole fraction of N in each sample. Since a linear correlation between peak area and N content would offer the best ability to quantify N across a range of concentrations, we fit linear trendlines. We evaluated the calibrations based on the slope (m) of the trendline, with high positive values indicating a greater sensitivity, and the R² scores indicating the goodness of fit. Given the relatively weak emission of N, we found that cropping the spectrum around the lines of interest and locally correcting the spectral baseline to linearity produced the best calibration. A similar approach was used for LIBS sulfur analyses [8]. Figure 1b-f shows a representative example of the series of calibration curves generated for each line (only the calibration for the 746.8 nm line is shown). Each salt series is plotted separately, but on axes with the same range, for clarity.

The calibration built on 742.4nm line (not shown) performed the worst overall, producing the shallowest slopes and lowest R² scores. The calibration from this line was particularly poor below 15wt% of the NO₃⁻ ion,

which calls into question the usefulness of this line for quantifying low N values. The average R^2 scores for the curves built on the remaining four lines are comparable and >0.9 , indicating that a robust linear correlation exists between these lines and N content. The curves made using the peak area at 746.8nm had the greatest analytical sensitivity to N content (steepest slope).

Effect of salt cation on N emission: In principle, the strength of LIBS emission depends on the number of atoms producing emission. However, we noted that N peak areas differed between some of the salt mixtures with identical mole fractions of N despite differences in total emission being accounted for by normalization. Further, regardless of which N line we considered, we observed consistent trends in the relative N emission intensity that coincided with the salt cation: the brightest lines emitted from samples with KNO_3 and the weakest lines from those with $\text{Mg}(\text{NO}_3)_2$. Indeed, some of the N lines we noted in our initial survey were uniquely undetectable in the samples of, or made with, $\text{Mg}(\text{NO}_3)_2$ (Table 1). This indicates that N emission from nitrate salts depends, in part, on the salt cation. Similar results were reported for salts of sulfur and chlorine [9] but the cause requires more research. The calibrations built on the 868.0nm line produced the highest average R^2 scores with the smallest degree of variability between salt species, suggesting this line is most robust to this effect.

Discussion: The ultimate goal of this work is to enable rapid stratigraphic mapping of mineralogical N on Mars' surface so that current and upcoming rovers can identify and explore astrobiologically important deposits of bioavailable N. We have identified four N lines that exhibit linearly increasing emission behavior with NO_3^- concentrations $>5\text{wt}\%$, highlighting their value for future quantitative analyses. A LOD of $5\text{wt}\%$ is higher than the NO_3^- content known on Mars [1], however, LIBS signals are stronger in the Martian environment [5], which may enable a lower LOD. We found that emission at 746.8nm has the greatest sensitivity of the four lines we considered and thus the greatest resolving power in distinguishing differences in N content, especially at low concentrations. We note that the tail of this line is partially overlapped by an unresolved quintet of O(I) lines contributed here by O in the NO_3^- ion and simulant material. On Mars, O from the CO_2 -rich atmosphere may challenge resolution of this line. We also found that absolute quantification of nitrate-N may be difficult as the calibration depends on the cationic composition of the salt, which is unlikely to be known *a priori*. We are currently working to understand both the nature of LIBS N emission under Martian conditions and the cation-anion relationship.

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References: [1] Stern J. C., et al. (2015) *Proc. Natl. Acad. Sci. U.S.A.*, 112. [2] Manning et al., (2008) *Icarus*, 197. [3] Harris R. D., et al. (2004) *Appl. Spectrosc.*, 58. [4] Dib et al., (2020) *Microchem. J.*, 157. [5] Cousin A., et al. (2011) *At. Spectrosc.*, 66, 805. [6] Cannon K. M., et al. (2019) *Icarus*, 317. [7] Kramida A., et al. (2018) *NIST Atomic Spectra Database (Version 5.6.1)*. [8] Dyar D. et al., 2004, *SAB*, 66. [9] Anderson D., et al., (2017) *JGR*, 122.

TABLE 1: N lines meeting initial identification criteria. Bold entries indicate lines most useful for detection given their presence at a wide range of N concentrations.

Wavelength (nm)					
742.4	818.8 ^a	824.2	865.6 ^{a,b}	870.3	905.0
744.2	820.2 ^b	856.8 ^b	868.0	871.2	906.0 ^b
746.8	821.1 ^b	859.4	868.3	871.9	938.7
818.5 ^a	821.6^a	862.9	868.6	904.6 ^b	939.3

^a Interference in high-Na samples from Na peaks

^b Not observed in samples of, or made with, $\text{Mg}(\text{NO}_3)_2$

FIGURE 1: Calibration curves built using integrated peak area of the 746.8 nm emission line for each salt series (b-f). Panel (a) shows an example of emission at 746.8nm showing increasing intensity with NO_3^- wt% (from KNO_3 series). Similar curves were generated for each of the 5 N lines deemed useful for detection.

