HOW DOES INSTRUMENT UNCERTAINTY AFFECT STOICHIOMETRIC IDENTIFICATION OF MINERALS IN THE JEZERO CRATER FLOOR? E. L. Moreland[1], K. L. Siebach[1], G. Costin[1], Y. Jiang[1], B. C. Clark[2], [1]Rice University, Houston, TX 77005 (morelandellie@rice.edu), [2]Space Science Institute (Boulder, CO 80301)

Introduction: Understanding mineral assemblages of rocks on planetary bodies can give crucial insights into the formation, evolution, and surface processes of rocky bodies [1]. Different techniques allow recognition and identification of various aspects of minerals; for example, X-ray diffraction provides a fingerprint of mineral structure and atomic spacing, whereas high-resolution chemical measurement techniques enable the identification of specific mineral formulae using stoichiometry. The Mineral Identification by Stoichiometry (MIST) algorithm is designed to recognize pure minerals stoichiometrically using high-resolution geochemical data [2]. Here, we present a technique for assessing the likelihood of identifying a particular mineral by stoichiometry alone when considering the analytical errors from a specific instrument. We then show how this technique allows us to assess our confidence in stoichiometric mineral identifications made by the Mars2020 Planetary Instrument for X-ray Lithochemistry (PIXL) instrument on the Jezero crater floor [3].

Methods:

High-Resolution Geochemical Instruments: Many instruments have been created to measure high-resolution geochemical data on Earth, and versions of these instruments have been configured to send to other planets. Each instrument has unique mechanics, data collection, and data interpretation processes that introduce uncertainties specific to the instrument. Here, we consider geochemical analyses and errors from three methodologies and instruments: Inductively coupled plasma–optical emission spectrometry (ICP-OES; 1-2 µm), Laser-induced breakdown spectroscopy (LIBS; ~100 µm), and PIXL (~120 µm).

MIST Algorithm: The MIST algorithm is a mineral identification algorithm exclusively based on geochemical stoichiometry, or testing whether element abundances and ratios could fit into a mineral structure assuming only one mineral was measured [2]. The algorithm takes high-resolution geochemical measurements and identifies when they fit within the known stoichiometric range of a mineral in the algorithm, accounting for allowed solid solutions, vacancies, and substitutions in real minerals. This method works when the monomineralic area is as large or larger than the measurement spot size so that the algorithm analyzes the chemistry of a pure mineral. The algorithm does not take analytical error into account.

Propagating Compositional Error using Monte Carlo: We use a Monte Carlo (MC) error propagation method to propagate the explicit uncertainty in the analytical analyses from the three geochemical instruments. This MC error propagation method was adapted from previous studies for repetitive calculations where the input data is randomly varied within the reported error range [4]. Applying an MC approach to our data creates a range of plausible mineral compositions based on the error reported by the instrument (Fig. A).

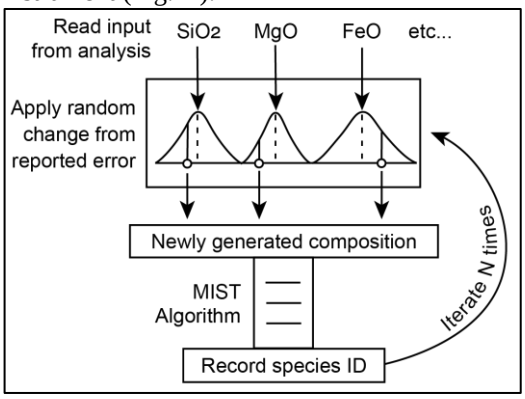

Figure A: Process schematic detailing the Monte Carlo (MC) method for producing repetitive calculations of mineral compositions given a reported error range.

"Reproducibility" Concept: We define a "reproducibility" parameter that estimates the likelihood of identifying a particular mineral by stoichiometry when the mineral chemistry has analytical errors. Direct incorporation of instrument error into MIST would be complex; different minerals have different tolerances for analytical error in different elements. Instead, for a given high-resolution measurement, a manual MC error propagation technique is used to generate a range of hundreds or thousands of compositions within the analytical error of the instrument used to make the measurement. All the synthetic compositions are input into the MIST model to identify how frequently the analyses accounting for analytical error are still recognized as the same mineral. The "reproducibility" of a mineral identification describes the percentage of times the same mineral is identified when error is incorporated through Monte Carlo error propagation.

Importantly, this "reproducibility" test favors minerals with compositions near the middle of the allowable range for that mineral and disfavors compositions near the edge of the acceptable compositional range. That means reproducibility does not directly assess the presence of a mineral; instead, it

assesses how well stoichiometry can identify a mineral given a particular mineral composition and error.

Comparing Example Mineral Reproducibility for Different Instruments: For a simple test of how the analytical instrument error affects the reproducibility of a mineral composition, we used five example mineral compositions and a simplified average error for each of the three analytical instruments. The minerals we use are olivine [$(Mg_{1.02}Fe_{1.00})Si_{0.99}O_4$], augite [$(Mg_{0.92}Ca_{0.80}Fe^{2+}_{0.27})Si_{2.00}O_6$], plagioclase feldspar [$(Na_{0.70}Ca_{0.30})Al_{1.3}Si_{2.7}O_8$], saponite [$(Ca_{0.16}Na_{0.04})(Mg_{2.43}Fe_{0.53})(Si_{3.19}Al_{0.94})O_{10}(OH)_2{\cdot}4H_2O$], and nontronite [$Na_{0.34}Fe^{3+}_{2.28}(Si_{3.42}Al_{1.14})O_{10}(OH)_2{\cdot}nH_2O$].

ICP-OES Instrument & Average Error: ICP-OES instruments determine the elemental composition of samples using spectral analysis of plasma generated from heating the sample. We use a standard error for ICP-OES as reported by Treiman et al. (2020) [4].

ChemLIBS Instrument & Average Error: The ChemLIBS instrument is a tabletop LIBS designed to be analogous to the Curiosity rover's ChemCam instrument [5]. LIBS uses a laser to vaporize a sample and analyzes the resulting plasma to obtain elemental composition. We use ChemLIBS standard error as reported by Dyar et al. (2016) [6].

PIXL Instrument & Average Error: The PIXL instrument is a micro-X-ray fluorescence spectrometer that uses X-ray fluorescence to determine elemental composition of analysis spots [3]. Our standard PIXL error averages all errors reported on measurements performed on the Jezero crater floor.

We test the five minerals with average error for each instrument by running our MC method with N = 5000. We then record the reproducibility of each mineral for each applied instrument uncertainty (Fig. B).

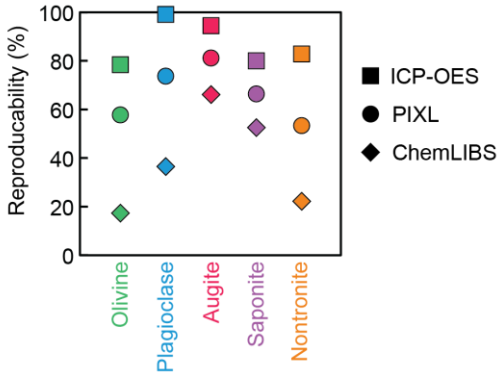

Figure B: Mineral reproducibility for selected mineral compositions by instrument using average reported instrument error. ICP-OES has the highest relative reproducibility values, while ChemLIBS has the relative lowest.

Mineral reproducibility across our three instruments shows that ICP-OES, with the smallest analytical error, achieves the highest reproducibility. ChemLIBS has higher errors on oxide analysis and thus produces the relatively lowest reproducibility for our minerals.

Reproducibility of Crater Floor Stoichiometric Minerals Identified by PIXL: We compile all MIST-identified points of five minerals from the nine PIXL scans performed in the Jezero crater floor: Guillaumes, Bellegarde, Dourbes (2 scans), Quartier (2 scans), Montpezat (2 scans) and Alfalfa. We perform MC with N = 1000 for each analysis spot using the unique error reported for the specific analysis point. We can then view each mineral's range of reproducibility values in the compiled crater floor data (Fig. C).

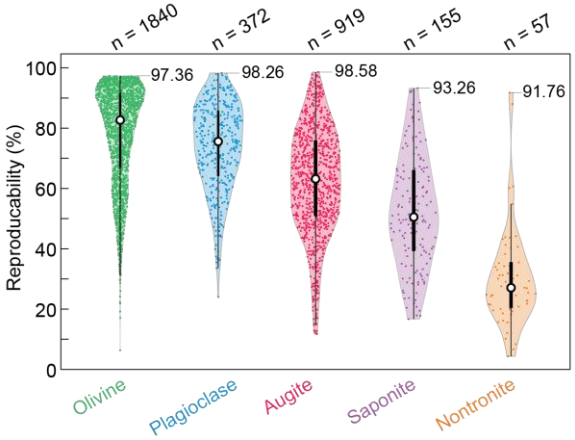

Figure C: Reproducibility of all analysis spots of each mineral in the Jezero crater floor PIXL data. Violin plots show the mean (white dot), first quartile (dark line), and third quartile (thin line) while also showing the density of data points.

The plots of reproducibility on the Jezero crater floor show that minerals with more simple stoichiometric formulas based on high concentrations of fewer elements (e.g., olivine and plagioclase) have higher reproducibility values compared to more complex minerals with higher ratios of error to element concentration (e.g., saponite and nontronite).

Summary & Implications: Here, we present a statistical approach to evaluate confidence in stoichiometric mineral identification given variable instrument errors. Our results show that confidence in stoichiometric mineral identification, assuming a monomineralic spot larger than the measurement spot size, depends on the instrument's reported analytical error and the mineral formula's relative complexity. These considerations are essential for evaluating mineral identifications on terrestrial bodies with different geochemical instruments.

References: [1] Hazen et al. (2023) JGR Planets 128(9). [2] Siebach et al. (2022) IMA Mtg. #OL40_5. [3] Allwood et al. (2020) Sp. Sci. Rev. 126(134). [4] Treiman et al. (2020) Plan. Sci. Journal 1(3). [5] Lepore et al. (2023) 54th LPSC #2806. [6] Dyar et al. (2016) Spectrochemica Acta B 123(93-104).