CALIBRATING PIXL FOR ELEMENTAL ANALYSIS ON MARS C.M. Heirwegh[1], Y. Liu[1], B.C. Clark[2], W.T. Elam[3], L.P. O'Neil[3], K.P. Sinclair[3], M. Tice[4], J.A. Hurowitz[5], A.C. Allwood[1], [1]Jet Propulsion Laboratory, California Institute of Technology, Pasadena, CA (Mail Stop 183-301, 4800 Oak Grove Drive, Pasadena, CA 91109, christopher.m.heirwegh@jpl.nasa.gov), [2]Space Science Institute, Boulder, CO, [3]University of Washington, Seattle, WA, [4]Texas A&M University, College Station, TX [5]Department of Geosciences, Stony Brook University, Stony Brook, NY.

Introduction: Across several Martian missions including Viking, Pathfinder, Mars Exploration Rover and Mars Science Laboratory, in situ planetary science investigations have been aided by the use of landers and rovers equipped with well calibrated X-ray fluorescence (XRF) spectrometers. XRF analysis can provide details of the inorganic geochemistry and elemental distribution of the Martian rocks and soils. Through use of these devices, planetary scientists seek to understand geological origins and past environmental conditions on a planet. They also use XRF to search for evidence of past habitability and now, with the Planetary Instrument for X-ray Lithochemistry (PIXL) on board NASA's Perseverance Rover, search for potential biosignatures in the rock record and inform the Mars 2020 rover mission on interesting samples worth caching for return to Earth on a future mission. Key to the efficacy of analyzing these data is the calibration of the instrument to constrain the accuracy of measuring elemental abundance in a target.

Described in detail elsewhere [1, 2], PIXL is a compact X-ray-tube-based XRF spectrometer that delivers a focused 120-micron diameter beam for interrogating the Martian surface. PIXL is also capable of raster scanning its beam to produce line, grid and contiguous whole map two-dimension images of elemental distribution for use in comparison to the visible images taken by PIXL's Micro-Context Camera.

Prior to flight, we conducted elemental calibration of the PIXL flight hardware to ensure that it met the design requirements concerning elemental quantification accuracy, element detection, and element detection limits. Our approach emulates calibration of the alpha-particle X-ray Spectrometers (APXS) flown on the earlier Mars rovers [3, 4] and was described in brief elsewhere [5]. While analysis of the calibration dataset collected with the PIXL flight hardware is ongoing (see below), we present here details on the calibration procedure and some results relevant to verification of the PIXL elemental quantification accuracy requirements.

Methods: Elemental calibration of the PIXL flight hardware was conducted at JPL in a simulated Martian environment (i.e. Mars gas at 6 Torr, -60°C). A calibration set consisted of: high-purity Teflon (PTFE), four glass reference materials (BHVO-2G, NIST 610, BCR-2G, BIR-1G), seven pressed-powder reference materials (LKSD-4, Gyp-B, COQ-1, SRM 694, SARM 6, Mica Mg and JMS-2) spanning an array of different geological material classifications. The calibration set also included several pure element and pure compound targets (NaCl, $MgCO_3$, Al_2O_3, SiO_2, ZnS, KBr, CaF_2, Ti, Fe, Ge, Y, Zr, $BaZrO_3$, CeO). In addition, the calibration pucks on the flight calibration target [1, 2] were measured to provide a reference for later measurements of these pucks during Mars surface operations.

Our calibration approach therefore adopts a 2-hour duration for measurement of each geological reference material, spaced out in a 3 x 3 grid of 0.5 mm spacing

Figure 1: PIQUANT fit (blue line) applied to the raw spectrum (dots) recorded from 4-hour integrated measurement of the Geological Survey of Japan's reference material (JMS-2). Key elemental constituents in the material are identified and the subtraction of data minus the bremsstrahlung background (bkgnd) is shown as the thin black line to help visually emphasize the presence of the peak. Note the y-axis is on log scale
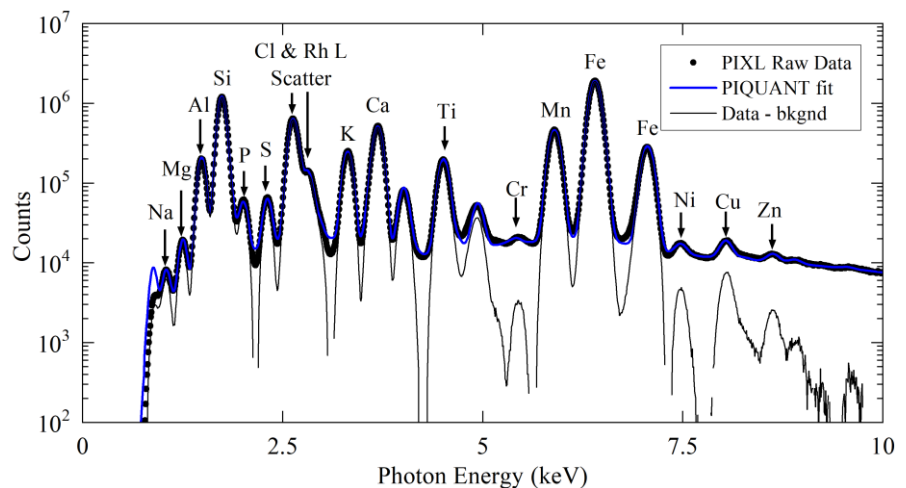
per spot to mitigate possible effects from sample inhomogeneities. Both detectors were used in the calibration, thereby rendering 4-hour total integrations of each material and spectral data such as that from the JMS-2 target, displayed in Fig. 1. Shorter durations (5 min) were used in the case of the pure elements and compounds since these materials are used to better define the element peak shapes.

Data were processed using our in-house dedicated PIXL physics fundamental parameters XRF quantification code (PIQUANT, [1]). Before quantification, we defined a photon transmission efficiency response as a function of photon energy for the PIXL focusing optic using the spectrum collected from Teflon [5]. Next, we used spectra from the glass targets to derive element-specific calibration factors (ECFs) to correct for inconsistencies in our spectrum fitting routine that can include, database issues, global peak fitting issues and, incomplete characterization of X-ray detector efficiency. Last, the transmission efficiency and the ECFs combined with hardware geometric were used to calculate the elemental abundances in wt.%.

Results: Quantification agreement between PIQUANT calculated element wt.% and certificate wt.% was obtained for 10 key major and minor elements, measured as percentage difference between the two values. Average deviations were calculated for each element as the root mean square error of deviation (RMSD) and compared to our L4 requirements, which mandate 10% accuracy levels at ~10 wt.% abundance for major elements (Mg, Al, Si, Ca, Fe) and ~1 wt.% abundance for minor elements (S, K, Ti, Cr, Mn). All elements met the L4 accuracy requirements with the exception of K and Cr, both of which presented RMSD spreads of 17%. Quantification of glass targets yielded an overall higher level of agreement with certificate values relative to the powder standards.

Discussion: The PIXL instrument meets or exceeds its requirements for quantification accuracy, as well as elemental detection and detection limit (not discussed here). The only exception is quantification accuracy for K and Cr (see below for possible causes and expected improvements). Overall, our performance with respect to accuracy is comparable to the most recent generation of XRF instrument flown to Mars (MSL APXS), and will enable the M2020 science team to confidently assess chemistry of bulk rock, rock components, and minerals to support accurate reconstruction of the geological history of different lithological units in Jezero crater.

We noted spreads in some elemental results, similar to those observed from calibrations of the MER [3] and MSL APXS [4] devices. The variation has been

attributed largely to the inhomogeneity of geo-reference materials [4]; this is an effect understood within the XRF community and associated with increased complexities of measuring often-non-homogeneous pulverized geo-reference materials. Pulverized geological reference materials were chosen in the calibration to cover the general range of compositions that might be observed on Mars.

For Cr and K, we anticipate improvements to quantification accuracy following a series of upgrades to PIQUANT currently in progress. It is also worth noting that all reference materials containing Cr possessed Cr in quantities much less than 1 wt.%, which increases the difficulty of quantification from such small peaks.

PIXL's experiments in the Mars 2020 surface operation will involve hundreds to thousands of spots, each typically lasting on the order of 10 s. Full elemental quantification of specified accuracy, however, requires integration of an X-ray measurement to last on the order of an hour or more. Thus, to realize quantification of unknown materials, several strategies may be implemented, including: 1) summing all spectra from a full X-ray map into one quantifiable spectrum, 2) sorting individual spectra from like mineral phases into summed single spectra representative of each phase, and 3) taking an extra-long duration single spot measurement of one location.

Future Efforts: PIQUANT upgrades include inclusion of low-intensity non-peak spectral features as part of the fitting code calculation to improve the accuracy of the peak area derivation. Upgrades also include adding incomplete charge collection tails to peaks on their low-energy edge, including physics-based effects on Compton escape in the detector and refining the physics model of the Rh X-ray tube emission profile. We will report on the re-analysis of our FM calibration dataset with the upgraded PIQUANT code. In addition, we plan to assess the flight instrument data against measurements performed on the same targets as well as an extended sample set using our in-house PIXL breadboard system. Further potential exists that we might develop a dedicated brassboard X-ray subsystem that would allow additional target measurements to be taken using flight-like hardware in a Mars-like environment.

References: [1] Allwood A.C., et al. (2020) *SSR, 216,* Article #134. [2] Allwood A.C., et al. (2021) *LPSC 52*. [3] Gellert R., et al. (2006) *JGR,* 111 (2006) E02S05. [4] Campbell J.L., et al. (2012) SSR, 170, 319 – 340. [5] Heirwegh C.M., et al. (2018) PDJ, 33, 162-165.