

PIXL ON PERSEVERANCE AS A COMPLETE X-RAY SPECTROSCOPIC INSTRUMENT: ANALYZING X-RAY FLUORESCENCE, SCATTERING, AND DIFFRACTION IN MARTIAN ROCKS. M. M. Tice¹, L. P. O'Neil¹, B. C. Clark², B. P. Ganly³, M. W. M. Jones⁴, B. J. Orenstein⁵, D. A. Flannery⁵, S. J. VanBommel⁶, M. E. Schmidt⁷, P. Nemere⁵, S. Davidoff⁸, A. Galvin⁸, C. Heirwegh⁸, W. T. Elam⁹, L. Wade⁸, A. C. Allwood⁸, and J. A. Hurowitz¹⁰, ¹Dept. of Geology & Geophysics, Texas A&M University, College Station, TX 77843, USA, mtice@geos.tamu.edu, ²Space Science Institute, Boulder, CO 80301, USA ³CSIRO, Glen Osmond, 5064, Australia, ⁴School of Chemistry & Physics and Central Analytical Research Facility, Queensland University of Technology, Brisbane, QLD 4000, Australia, ⁵School of Earth & Atmospheric Sciences, Queensland University of Technology, Brisbane, QLD 4000, Australia, ⁶McDonnell Center for the Space Sciences, Department of Earth and Planetary Sciences, Washington University of St. Louis, St. Louis, MO 63130, USA, ⁷Department of Earth Sciences, Brock University, St. Catharines, ON L2S 3A1, Canada, ⁸Jet Propulsion Laboratory, California Institute of Technology, Pasadena, CA 91109, USA, ⁹Applied Physics Laboratory, University of Washington, Seattle, WA 98105, USA, ¹⁰Department of Geosciences, Stony Brook University, Stony Brook, NY 11794-2100, USA.

Introduction: The PIXL instrument (Planetary Instrument for X-ray Lithochemistry) [1] on the Mars 2020 *Perseverance* rover payload provides co-aligned capabilities for x-ray fluorescence, multi-spectral VNIR imaging, and limited x-ray diffraction, at spatial scales ranging from ~50 μm (PIXL VNIR image resolution) to ~120 μm (PIXL x-ray spot size at 8 keV) across areas up to ~17.6 cm^2 . Typical PIXL observations include continuous XRF maps over rectangular areas up to $4 \times 12.5 \text{ mm}^2$, 1-3 lines up to 36 mm, and square grids up to $22 \times 22 \text{ mm}^2$. PIXL data have demonstrated compositional and crystallographic variations with significant implications for rock formation and alteration mechanisms in Jezero crater floor rocks [2-4].

PIXL's dual-detector configuration allows automated comparison of x-ray spectra acquired at two orientations to the target. This capability was previously used to identify and map diffraction peaks [2,3]. We show here that PIXL data can also be used to map target topography, correct quantified oxide abundances for slope and diffraction artifacts, map and quantitatively analyze diffraction patterns, and quantify the intensity of backscattered x-rays. Finally, we demonstrate routines for quantification and subtraction of dust coatings as well as carbonate minerals within targets. All data treatment and visualization routines are implemented in the open-source PIXLISE expression environment [1,5].

Topographic Slope: X-ray fluorescence observed from a surface follows Lambert's Cosine Law, $I = I_0 \cos \varphi$, where φ is the angle between the detector and the surface normal. We show that the relative difference in intensities observed by detectors A and B, $\varepsilon = (I_A - I_B)/(I_A + I_B)$, is a function of topographic slope in the vertical plane connecting the detectors [6].

Slope and Diffraction Corrected Abundances: All but a small fraction of diffraction peaks in PIXL spectra can be identified as systematic differences in slope-adjusted photon counts between detectors. We show that improved analytical totals and material

identifications are achieved by ignoring oxide quantifications from detectors where diffraction affects the most intense fluorescence peak for the associated element, and by rescaling remaining abundances to correct for slope (**Fig. 1A,B**). Topographic and roughness effects contribute analytical uncertainty in absolute elemental abundances comparable to or greater than calibration uncertainty on flat, smooth targets. Slope and roughness do not significantly contribute to uncertainty in elemental ratios.

Diffraction Patterns: The presence or absence of multiple diffraction peaks in separate spectra from detectors A and B reflect target mineral identity, the presence and size of coherent crystalline domains, and crystallographic orientation [2,3]. We demonstrate that a mapping of automatically detected diffraction peaks to 4-, 8-, and 16-bit integers provides a rapid technique for visualizing distinct diffracting grains (**Fig. 1C**), analyzing contacts and alteration profiles in and around grains, estimating average coherent crystalline domain sizes, and identifying long-range correlations (e.g., from poikilitic or poikilotopic textures).

Backscatter Intensity: After correcting for roughness and diffraction effects, backscattered photons from the PIXL x-ray source can be mapped across rock surfaces. We show that backscattered intensities reflect a combination of sample density and the relative cross sections for photoelectric absorption versus Rayleigh scattering. Backscatter intensity profiles provide information about composition that is complementary to that derived from observable elemental fluorescence (**Fig. 1D**).

Dust Quantification and Subtraction: Thin (up to a few 10s of μm) and/or spatially heterogeneous layers of dust can be partially penetrated by x-rays from PIXL, and some fluorescence from underlying rocks can escape and be detected. The efficiency of fluorescence generation and detection through dust depends on dust thickness, patchiness, composition, and (to first order) on the atomic number of the element being detected. We

demonstrate a routine which estimates the maximum amount of dust which could be present in an analytical spot, assuming a Jezero average dust composition. This routine is based on a model of x-ray transmission through thin dust layers. We find that it effectively maps dust on natural surfaces and produces reasonable estimates of composition in underlying rocks.

Carbonate Mineral Stripping: Mathematically removing minerals with distinctive compositions and simple stoichiometries (e.g., spinels, phosphates) from analytical spots is an effective tool for simplifying multi-mineral mixing arrays in PIXL data [3]. We demonstrate that the intensity of low-energy backscattered x-rays correlates with inferred matrix CO_2 in several PIXL targets, and that carbonate minerals can be mapped and stripped in these targets. In combination with quantifying selected analytical spots using a carbonate matrix rather than an oxide matrix, this approach improves mineral identification and element ratio estimation.

Summary: The data analysis techniques described here demonstrate that the PIXL instrument, originally designed as a mapping XRF microscope, has significant enhanced analytical capabilities that result from its specific design features, enabling analysis of topography, crystallography, carbonate/ H_2O , and dust, and the effects of these factors on XRF datasets.

Acknowledgments: PIXL images and data used in this paper are available on the Planetary Data System (PDS; doi:10.17189/1522645). Contributions by JPL co-authors were funded under contract with the National Aeronautics and Space Administration (80NM0018D0004).

References: [1] Allwood A. C., et al. (2020) *SSR*, 216, Article #134. [2] Liu Y., et al. (2022) *Sci.*, 377, 1513–1519. [3] Tice M. M. (2022) *Sci. Adv.*, 8, eabp9084. [4] Farley K. A., et al. (2022) *Sci.*, 377, eabo2196. [5] Heirwegh C. M., et al. (2022) *Spectrochim. Acta B*, 196, 106520. [6] Smilgies D. M., et al. (2012) *J. Synchrotron Radiat.* 19, 547–550.

Figure 1. **A)** Uncorrected compositional map of the “Dourbes” abrasion patch from the Séítah formation [2-4] showing relative molar proportions of $\text{MgO} + \text{FeO}$, $\text{CaO} + \text{Na}_2\text{O} + \text{K}_2\text{O}$, and SiO_2 . Major components labeled (ol=olivine, pyr=pyroxene, mes=feldspathic mesostasis, carb=carbonate, sulf=sulfate). Arrow indicates olivine grain apparently enriched in Na_2O . **B)** Compositional map as in (A), but adjusted to correct for artifacts from slope and diffraction. Arrow shows olivine grain with no Na_2O enrichment; in this case, a diffraction peak produced by crystalline olivine overlapping the Na K peak has been removed. **C)** Diffraction peaks detected by det A (red), B (blue), and both A and B (green) coded as 4-bit integers. Different diffraction patterns map to different colors, allowing quick identification of coherent crystalline domains with the same patterns. **D)** Backscattered x-ray intensities integrated from 9.17-12.42 keV (red; “High-E”), 2.46-2.95 keV (green; “Rh”), and 5.50-5.62 keV (blue; “Cr”). Scattering profiles reflect varying compositions, backscattered Rh intensity indicates carbonate minerals.

