

PRIMARY DEPOSITIONAL AND SECONDARY DIAGENETIC FABRICS IN EVAPORITE ROCKS AS SEEN BY PERSEVERANCE ROVER'S PIXL INSTRUMENT. M. J. Meyer¹, R. E. Milliken¹, J.A. Hurowitz², and K. M. Robertson¹, ¹Dept. Earth, Env., and Planetary Sciences, Brown University, Providence, RI 02912, Dept. Geosciences, Stony Brook University, Stony Brook, NY 11794. melissa_meyer@brown.edu.

Introduction: On Earth, accurately constraining the ancient environments and mechanisms that shape a particular sedimentary rock is not always entirely straightforward. Disentangling primary depositional features from post-depositional diagenetic and surficial weathering processes often requires meticulous field and laboratory investigations. Rover missions have revealed that the stratigraphic record of Mars is comparably complex and rife with a diverse range of primary lithologies, secondary diagenetic textures, and erosional geomorphologies [1-5]. Moreover, unambiguously relating measurements of chemistry and mineralogy to particular attributes (e.g., grains, cements, concretions, veins, etc.) in a given sedimentary rock has proven to be challenging due to the instrument limitations of *Opportunity* and *Curiosity* Rovers [3,6].

Perseverance Rover's Planetary Instrument for X-Ray Lithochemistry (PIXL) will likely be capable of resolving elemental variations associated with these types of geologic features to an unprecedented resolution on Mars. As described in [7], PIXL is a micro x-ray fluorescence (XRF) mapping instrument that utilizes induced fluorescence from a 0.12 mm-diameter focused x-ray beam to produce spatially customizable elemental point, line, and map measurements. The sensor components of PIXL are mounted on the turret at the end of *Perseverance*'s robotic arm and include a high flux x-ray source, a pair of x-ray detectors, and a camera for spatial referencing. The device is capable of self-adjusting in the z-direction in order to follow rock surface roughness, maintain a consistent stand-off distance between measurements, and create a quantitatively comparable data set on a given rock surface.

In order to assess PIXL's ability to resolve key textural and diagenetic characteristics within sedimentary rocks, we examined four mixed siliciclastic-evaporite samples (Fig. 1) from the Rocky Arroyo outcrops of the Seven Rivers Formation near Carlsbad, NM [8]. Here we compare breadboard PIXL measurements with variations in petrographic textures, XRD mineralogy, and near-IR point and imaging spectroscopy.

PIXL Measurement Methods: Measurements were collected on whole-rock samples using the breadboard PIXL instrument at Stony Brook University. This instrument has several notable differences to the instrument incorporated into *Perseverance* Rover's payload. The breadboard PIXL is not equipped to adjust in the z-direction or correct for sample topography and therefore requires the analysis of relatively flat samples. Unlike the PIXL aboard *Perseverance* Rover, the breadboard version requires operation under helium purge in a laboratory setting in order to reduce atmospheric scattering and to better detect light elements. The breadboard

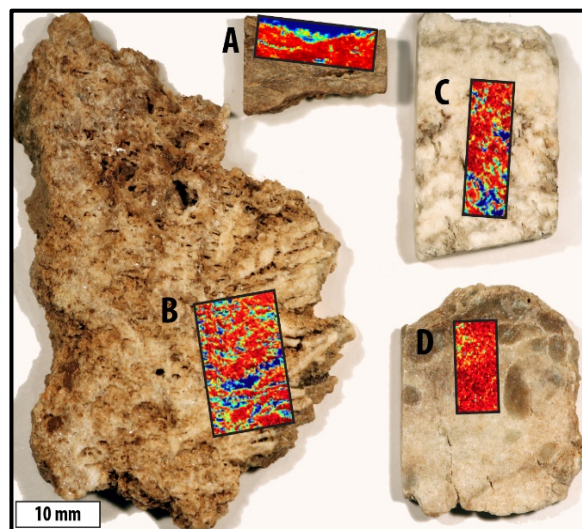


Fig. 1: Seven Rivers Formation evaporite samples analyzed in this study showing footprint measured by PIXL and raster overlay of Ca content for each sample (color bar for Ca shown in Fig. 2). Customized dimensions for each scan: (A). 15 mm x 4.65 mm grid size, 3232 total spectra, 12.6 hour collection time; (B). 15 mm x 9.9 mm grid size, 6767 total spectra, 26.2 hour collection time; (C). 15 mm x 4.95 mm grid size, 3434 total spectra, 14.3 hour collection time; (D). 9.9 mm x 4.95 mm grid size, 2278 total spectra, 8.6 hour collection time.

PIXL also does not have a context camera to provide positioning information. PIXL measurements taken in this study are therefore integrated with independently acquired high-resolution photographs.

For each complete scan (Fig. 1), a flat sample was placed on a motorized mechanical stage beneath the breadboard's stationary x-ray beam and detectors. The motorized stage was programmed to move at a 150 μ m step size across a customized x-y dimension for each sample (see Fig. 1 caption). Prior to completing the scan, samples were manually adjusted in the z-direction to a standoff distance of 25 mm from the x-ray beam. A 10 second dwell time to collect and integrate spectra was utilized for each individual measurement across all samples.

Resultant spectra were processed using PIQUANT, a fundamental parameter based XRF software developed specifically for quantification of PIXL XRF spectra [7]. Peaks for the following elements were manually identified in bulk measurement spectrum and used to quantify elements in each individual x-ray spectrum: Si, Ti, Al, Cr, Fe, Mn, Mg, Ca, Na, K, S, Cl, P, and Sr.

Other Laboratory Methods: For all powdered analyses, samples were ground with a mortar and pestle

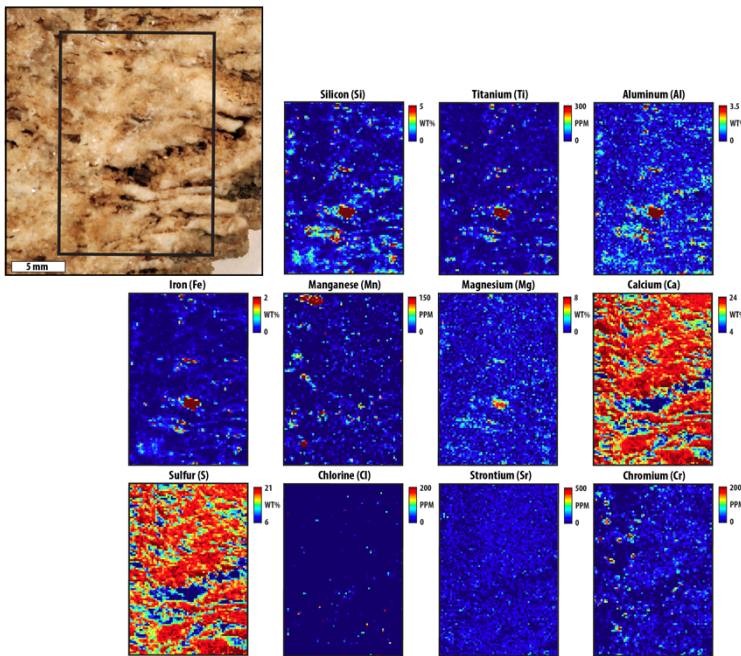


Fig. 2: Spatially mapped PIXL measurements for 11 identified elements in sample B (see Fig. 1 for map location on sample).

and hand sieved to a particle size of $< 45 \mu\text{m}$. Powdered X-ray diffraction (XRD) measurements were collected on all samples using a benchtop Bruker D2 Phaser with a Cu-K α x-ray source.

An Analytical Spectral Devices (ASD) FieldSpec3 spectrometer was used to collect reflectance spectra in the visible-near infrared wavelength region (0.35 to $2.5 \mu\text{m}$) relative to a white Spectralon diffuse standard. A Thermo Nexus 870 FTIR spectrometer was used to collect reflectance spectra in the near-mid infrared wavelength region (1.5 to $25 \mu\text{m}$) relative to a diffuse gold standard.

Results: Samples retaining primary bedding characteristics (e.g. sample B, Fig. 2) are dominated by fine-grained, light-toned, wavy-discontinuous primary gypsum laminations interbedded with secondary amounts of wavy-discontinuous dark-red silt laminations. These dark-toned silt laminations are interpreted to be sourced from wind-blown dust particles deposited via suspension settling in an evaporitic backreef lagoon [8].

XRD measurements indicate that the light-toned matrix of these samples is dominated ($>90 \text{ wt}\%$) by gypsum with secondary amounts of apatite and dolomite. In contrast, silt laminations contain a wide variety of major and trace phases including most notably quartz, albite, muscovite/illite, montmorillonite/smectite, chlorite, and hematite. Only when physically separated from the light-toned gypsum laminations are spectral contributions from the phyllosilicate- and hematite-bearing silt particles perceptible in reflectance measurements; bulk point spectral measurements lack clear evidence of clay-bearing silt and are instead dominated by spectral contributions from gypsum.

While the presence of compositionally distinct silt laminations is subtle in whole-rock XRD measurements

of mineralogy and imperceptible in whole-rock spectral measurements, they are readily identified by PIXL mapping (Fig. 2). Light-toned primary gypsum laminations clearly correlate to distinctly higher concentrations of S and Ca. Dark-toned primary silt laminations clearly correlate to distinctly higher concentrations of Si, Ti, Al, Fe, K, and Mg. Silt with aggregated particle sizes of $300 \mu\text{m}$ (\sim two pixels in a PIXL image) or greater can be detected and visually correlated with confidence.

PIXL mapping also captured micro-scale chemical changes across diagenetic boundaries present in the samples that are otherwise imperceptible by XRD and spectroscopic analytical techniques. Late-stage diagenetic gypsum-recrystallization is observed to crosscut primary laminations in sample B. Gypsum-recrystallized portions (upper left corner of PIXL scan, Fig. 2) contain significantly less silt particles (silt presence is inferred by co-increases in Si, Ti, Al, Fe, K, and Mg concentrations and by visual inspection). Millimeter-scale Cr and Mn nodules are also observed in the recrystallized portion of the sample. In sample D (Fig. 1), PIXL reveals a variety of chemistries—discrete enrichments in Mn, Cr, and Ti—in mm-scale nodules that would otherwise appear homogenous in chemical composition. PIXL also maps subtle changes in Sr across fracture fills and Cl across small halite inclusions (samples C and D). The presence of these diagenetic features often is distinguishable in thin section images but remain ambiguous in hand sample photographs and are unresolvable by XRD measurements and reflectance spectroscopic techniques.

Implications for Perseverance Rover: *Perseverance* Rover's PIXL instrument is capable of mapping subtle micro-scale variations in primary bedding composition that could not be unambiguously detected in whole-rock measurements of mineralogy, chemistry, or reflectance. PIXL also clearly captures chemical variations associated with diagenetic nodule and fracture formation. *Perseverance* Rover is expected to encounter a variety of sedimentary rock types in Jezero Crater. Compositional variations due to both primary and secondary characteristics in these rocks may exhibit comparable spatial heterogeneity to that of the siliciclastic-evaporite samples studied here. PIXL is a promising tool for quantifying these variations and will likely aid in transcribing the Martian rock record to an unprecedented level.

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