**LABORATORY MEASUREMENTS OF SURFACE LAYERS AND COATINGS WITH PIXL.** S. J. VanBommel[1], A. L. Knight[1], J. A. Hurowitz[2], N. L. Lanza[3], and A. M. Ollila[3]; [1]Washington University in St. Louis, St. Louis, MO, USA; [2]Stony Brook University, Stony Brook, NY, USA; [3]Los Alamos National Lab, Los Alamos, NM, USA.

**Introduction:** The Planetary Instrument for X-ray Lithochemistry (PIXL) onboard the Mars 2020 rover *Perseverance* utilizes an active X-ray source and twin silicon drift detectors to analyze geologic materials on Mars [1]. X-ray fluorescence (XRF) interrogation of geologic specimens on Mars, in particular natural surfaces analyzed in situ, are prone to numerous challenges that typically do not encumber a terrestrial laboratory setting [2]. *Perseverance* includes a coring mechanism to facilitate Mars Sample Return efforts, as well as an abrasion bit to grind away surface material to mm-depths, after which the tailings are largely expelled using compressed gas (via the gDRT) [3, 4]. The abrasion bit and compressed gas system are used in tandem to prepare smooth, dust-free surfaces for both PIXL and another turret-mounted instrument, SHERLOC, a Raman spectrometer with imaging capabilities [4, 5].

Abrading surfaces removes the uppermost several mm of material. While this does present a (largely) smooth and flat surface for PIXL (and SHERLOC) to analyze, it also removes any potential surface coatings and subsequential information that can be gleaned from analysis (e.g., [6]), including possible biosignatures (e.g., [7]). PIXL's hexapod and optical systems enable it to safely maneuver itself within a constrained area at a fixed distance from the surface [1], mitigating to some degree the effects of surface roughness and variable target relief that are present on natural surfaces.

Here we present measurements conducted using the PIXL breadboard (BB) at Stony Brook University (SBU) of synthetic and natural samples with coatings and discuss their ability to help inform observations conducted on Mars by *Perseverance*. The data will ultimately help calibrate ongoing PIXL layer modeling efforts (e.g., [8]) based off fundamental X-ray physics theory (e.g., [9]). As the mean sampling depth for a given elemental line increases with X-ray energy (and therefore atomic number), analyses of coatings a dozen or two µm thick with XRF instruments result in counts that are skewed to the coating for low-Z elements and to the substrate for high-Z elements. This necessitates the need for a comprehensive layering analysis routine to fully characterize potential coatings or layered samples on Mars, including *infinitely thick* samples under a layer of Mars dust (e.g., [8, 10]).

**Method:** The SBU PIXL BB consists of a similar source and detector configuration as that of the PIXL flight instrument currently on Mars. The instrument is mounted within a glovebox that is kept at ambient pressures but can be purged with helium; at first order, 1 atm He gas has a similar X-ray cross-section to ~1 mbar $CO_2$ (simplified Mars atmosphere).

A suite of samples were measured, including synthetically-created and naturally-occurring (Mn) coating specimens provided by Los Alamos National Lab, which had previously conducted characterization efforts. These efforts included laser-induced breakdown spectroscopy (LIBS) analyses with the SuperCam analog instrument, not only enabling future cross-instrument analyses of these data, but also improved joint characterization of potential coating targets observed on Mars.

The scope of the SBU PIXL BB analyses was expanded through the use of Al-coated samples. Numerous samples and calibration standards were layered with standard household Al-foil (nominally ~16 µm thick) and measurements taken to characterize changes in the observed spectra while incrementally increasing the number of layers. Analyses were also conducted on a 2014 United States penny which consists of 20 µm Cu cladding on a Zn core. The high-Z nature of both elements, and the Cu K-edge being above the Zn $K_\alpha$ line, complement the rest of the sample set, especially as the number of Al layers increased. Experiments were also conducted to constrain the effects of helium leakage from the glovebox with time (i.e., characterize the rate of Earth atmosphere bleed in – important due to its impact on spectra, especially lower energy signals) through monitoring the Earth-atmosphere-sourced Ar signal in each spectrum.

**Results and Discussion:** Early layer modeling efforts focusing on the PIXL instrument suggest the sampling depth for PIXL (or a PIXL BB) is shallower than that of analyses conducted by the Alpha Particle X-ray Spectrometer (APXS) on *Curiosity* or those on either of the Mars Exploration Rovers [8]. This is due to the continuum of the incident X-ray energies from PIXL, peaking around 3 keV, whereas APXS utilizes a combination of 5.2 MeV $He^{2+}$ ions and 14+ keV X-rays to interrogate samples [11]. The penetration depths for the $He^{2+}$ ions and 14+ keV X-rays exceed the escape depths of the characteristic X-rays of interest, which therefore are the depth-determining factor for APXS analyses. Shallower mean sampling depths on PIXL further emphasize the importance of a comprehensive analytical layering model.

Lab spectra of Al foil on BCR-2G are presented in Figure 1 and Al foil on the penny in Figure 2. Al cps are saturated after one Al layer (~16 µm), as expected, given the projected 90% escape depth of Al X-rays (~4 µm; e.g., [6, 8]). Subsequent layers further attenuate counts from higher-Z elements. Peak area ratios as a function of Al layer thickness are illustrated in Figure 3 for various materials analyzed by the SBU PIXL BB.

On sol 463 *Perseverance* deployed PIXL to scan a rock named "Pignut_Mountain" after it was shot with the SuperCam LIBS laser. A PIXL three-line scan was conducted perpendicular to the line of LIBS points. As the SuperCam activity redistributed the dust into a halo-shaped pile around the line of LIBS points, the PIXL scan transected three distinct regions: a region of exposed relatively dust-free rock, a region of dust piled up from the LIBS activities, and a natural unaltered region. Combined with analyses of the PIXL calibration target hardware (e.g., [12]), Pignut_Mountain data presented the opportunity to explore the thickness of dust through layer modeling when comparing the spectra of the bare and natural surfaces. Preliminary analyses suggest dust on the order of 10-20 µm thick is present on the natural surface, consistent with earlier measurements elsewhere on Mars (e.g., [13]).

**Summary and Future Work:** Laboratory measurements with a PIXL analog instrument, combined with flight instrument analyses of dusty calibration targets and post-LIBS rock surfaces, provide a library of spectra to calibrate PIXL layer analysis models currently under development. The verification of these models will enable PIXL to better constrain the properties of potential surface coatings it encounters and mitigate the effects of dust on natural surfaces. The ultimate goal is the integration of these models into PIXL's analytical routines to enable the rapid analysis of coating targets encountered. The joint use of PIXL layer models and LIBS depth profiles only further enhances *Perseverance*'s coating analysis capabilities (e.g., [6, 14]).

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**References:**

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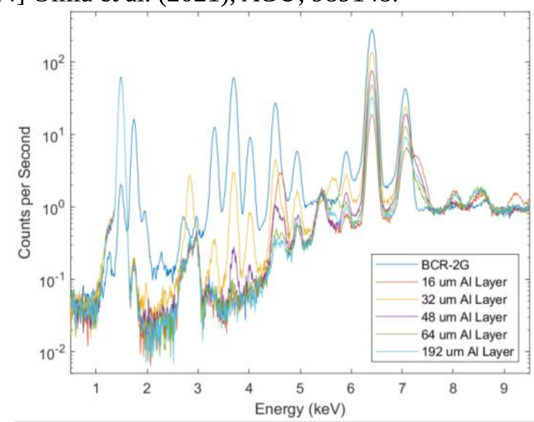


**Figure 1:** Layered aluminum foil on BCR-2G.

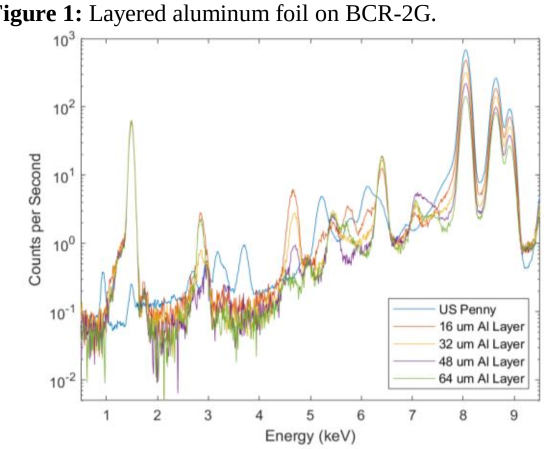


**Figure 2:** Layered aluminum foil on a 2014 US penny.

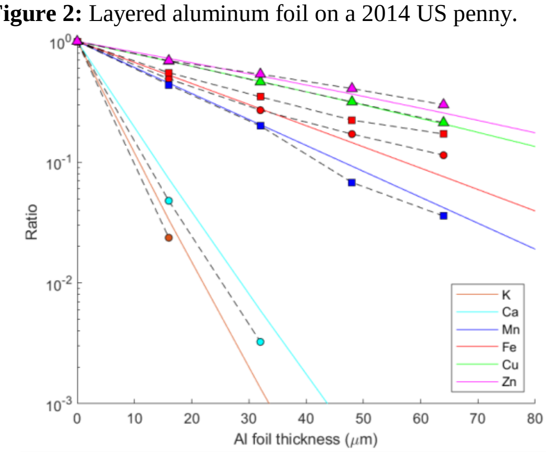


**Figure 3:** Peak area ratios as a function of Al foil thickness. Points correspond to laboratory measurements (circles = BCR-2G, squares = pure Mn, triangles = US penny) and lines to predictions based on a simplified model utilizing the incident flux profile of PIXL. For the penny, predicted Cu values are within 1% through 48 µm and 3% through 64 µm, while predicted Zn values are within 5% through 32 µm but low by 10% and 15% at 48 and 64 µm respectively. Deviation between observed and predicted as cumulative sampling depth approaches unity is not unexpected due to limitations of the current model including its lack of correcting for secondary effects and the application here of a fixed substrate.