

Texture-specific elemental analysis of rocks and soils with PIXL: The Planetary Instrument for X-ray Lithochemistry on Mars 2020

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Abstract— PIXL (Planetary Instrument for X-ray Lithochemistry) is a micro-focus X-ray fluorescence instrument for examining fine scale chemical variations in rocks and soils on planetary surfaces. Selected for flight on the science payload for the proposed Mars 2020 rover, PIXL can measure elemental chemistry of tiny features observed in rocks, such as individual sand grains, veinlets, cements, concretions and crystals, using a 100 μm -diameter, high-flux X-ray beam that can be scanned across target surfaces.

At the heart of PIXL, a polycapillary X-ray focusing optic focuses the X-ray beam down to a $\sim 100\mu\text{m}$ spot. The optic is coupled to a state-of-the-art miniature microfocus X-ray tube. The X-ray beam produced by the focused X-ray source yields extremely high fluorescent X-ray count rates, enabling sensitive analysis of each spot in a few seconds. In 5-10 seconds, PIXL reveals major and minor elements in a sample. In 1 to 2 minutes, sensitive trace element analysis is achieved. Different measurement strategies allow flexibility during operations to respond to scientific opportunities and resource constraints. PIXL can perform line or grid measurements on abraded or natural (unabraded) surfaces.

With operational flexibility, high spatial resolution, high sensitivity, a wide range of detectable elements, rapid spectral acquisition and a raster scanning capability for chemical mapping, PIXL would enable detailed insights to past habitability and the potential for preservation of biosignatures.

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1. INTRODUCTION

Making close-up measurements of the elemental chemistry of rocks is a fundamental capability for surface-based

exploration of rocky planets. Accordingly, almost every landed Mars mission since the Viking lander in 1976 has had an X-ray fluorescence (XRF) instrument for measuring the elemental chemistry of rocks and soils. However, to date the emphasis has been on measurement of bulk composition across a relatively large area (17mm diameter for the Alpha Proton X-ray Spectrometer on the Mars Science Laboratory's Curiosity rover). Achieving much finer spatial resolution measurements is important for measuring chemical variation among (sub)millimeter-scale features such as grains, layers, veins, spherules, crystals, coatings and cements that make up the rocks. These fine scale features hold important clues to past habitability and the potential for preservation of biosignatures in rocks. In particular, integrated assessment of fine scale textures and chemical variations is important for identifying and evaluating geologic features of potential microbial origin, and determining whether they are indeed biogenic.

To that end, we developed PIXL (Planetary Instrument for X-ray Lithochemistry): a micro-focus X-ray fluorescence instrument for examining fine scale chemical variations in rocks and soils on planetary surfaces. PIXL has been selected to fly aboard NASA's proposed Mars 2020 rover mission, where it would be mounted on the rover's robotic arm for close-up examination of rock and soil targets. Here we describe the PIXL instrument, illustrate the utility of PIXL's micro-XRF measurements with example results from the analysis of astrobiologically significant geological features with a PIXL flight prototype (Figure 1).

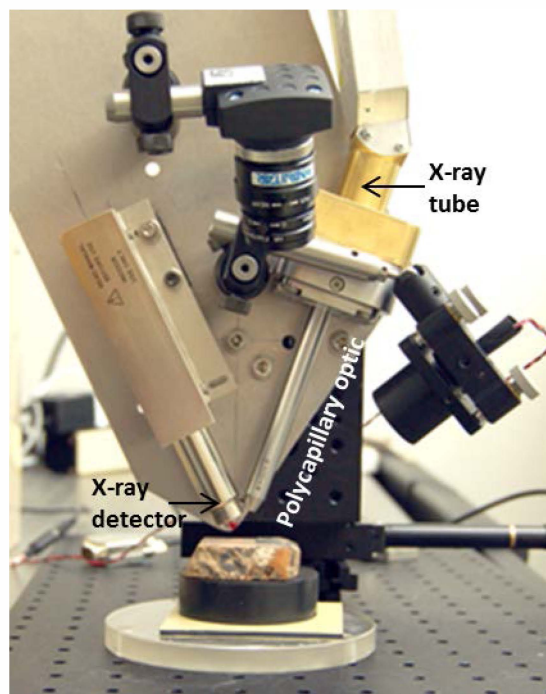


Figure 1 - The PIXL breadboard instrument, which consists of commercial components mounted on a plate attached to X-Y stages. This breadboard has performed more than 750 000 integrations over more than 5,000 hours. The spectra were acquired from hundreds of

rocks, minerals, powders and reference materials over a wide range of voltages (10–50 keV) and currents (1–200 μ A). For scale, rock sample is approximately 1cm thick.

2. MICRO-FOCUS X-RAY FLUORESCENCE PRINCIPALS AND APPLICATIONS

In XRF spectroscopy, X-rays from a source hit the surface of a sample, causing the sample to fluoresce over the illuminated area (the analytical spot). The energies and numbers of emitted fluorescent X-rays are determined by the sample's elemental composition. Emitted X-rays are counted and their energy measured using a semiconductor detector. Upon striking the detector, an X-ray photon produces a number of electrons proportional to the photon energy. Readout electronics convert this charge into a voltage pulse and measure the height of the pulse. A multi-channel analyzer counts the number of pulses having a given pulse height. The resulting histogram of pulse count vs. pulse height is calibrated to create an X-ray spectrum. Peak position on a spectrum identifies the element and the peak intensity reflects the abundance of the element.

Where the X-ray beam illuminates a heterogeneous sample, all the elements contained in the different phases are combined in a single spectrum. To separately measure the different phases, a smaller analytical spot is required. Conventionally, a smaller analytical spot is achieved by placing a pinhole in front of the X-ray source, which blocks much of the radiation from the X-ray source in order to illuminate a limited area on the surface of the sample. The disadvantage of pinholes is low X-ray flux and concomitantly long integration times to achieve the desired analytical sensitivity. Recent advances in X-ray focusing optics enable high spatial resolution XRF measurements of sample surfaces without significant loss of flux [1]. Polycapillary focusing optics take advantage of grazing incidence reflection of X-rays. X-ray photons that strike a smooth glass surface, with an angle not greater than 0.1° , will be reflected. By shaping the surface such that a series of reflections occur, it is possible to bend X-rays through a large angle. By combining many such surfaces in a polycapillary optic, divergent X-ray photons from a source can be collected over a significant solid angle and then reflected so that a tight focus is achieved. Focusing results in both small spot size and high X-ray flux. Polycapillary optics consist of millions of $10\text{ }\mu\text{m}$ -diameter glass capillary tubes fused together in a monolithic close-packed array structure. Optic diameter, degree of taper, focal length and number and length of capillaries are customized to produce the desired output spot size. In the case of PIXL, the output spot diameter is $100\text{ }\mu\text{m}$ at the focal point. The X-ray flux density at the focal point of PIXL's polycapillary optic is 140 times higher than the same X-ray tube output flux through a $100\text{-}\mu\text{m}$ pinhole. This high flux means only short integration times are needed to measure the chemical composition with acceptable sensitivity. This, in turn, means the beam can be rapidly moved from spot to spot in order to build up an elemental map over a large area.

Micro-XRF has been used for materials characterization in a variety of scientific and commercial applications, such as art and archaeology, forensics, electronics, microbiology, and many others [2]. In geology, a micro-XRF instrument like PIXL can be used to map the distribution of chemical elements relative to physical components such as grains, layers, cements and crystals that make up the rocks, in order to determine the origin and history of the rocks. This capability is the essence of petrology. Although micro-XRF is only recently emerging as a valuable petrologic tool, the basic concept of texture-specific element mapping is very familiar to petrologists, who commonly use energy dispersive X-ray spectroscopy (EDS) in electron microscopes to map elements relative to textures at micron scales in rocks. By observing how elements group together spatially, petrologists can identify or constrain the minerals present, and their spatial distribution and relationships. Micro-XRF can be used for the same kinds of petrologic measurements but on a larger scale, covering surface areas up to several square centimeters with sub-millimeter-scale resolution.

This scale of observation is similar to that of a geological hand lens, which is one of the most fundamental tools for studying outcrops and hand samples in field-based geological investigations. Observations at the hand lens scale bridge the gap between large scale techniques (kilometer scale airborne or orbital remote sensing observation to meter-scale outcrop observations) and high resolution laboratory techniques (microscopy, EDS, etc at micron and smaller scales). Micro-XRF provides chemical information at this important intermediate scale, making it an effective technique for analyzing hand samples or outcrops in field-based investigations, including robotic field work on Mars.

3. ADAPTING MICRO-XRF FOR FLIGHT

Micro-XRF is amenable to implementation on a rover or lander both because of the relatively limited sample preparation and pointing/positioning requirements placed on the spacecraft and because the key technologies – X-ray tubes and polycapillary optics – are inherently small, lightweight, low power and rugged. The PIXL instrument combines these new technologies with high-heritage flight components to form a compact, rugged and scientifically powerful instrument for the Mars 2020 rover mission.

PIXL has three parts: an arm mounted sensor head, electronics in the body of the rover and a calibration target mounted on the rover exterior. The components of the sensor head are grouped into two main subsystems: the X-ray Assembly (XRA) and Optical Fiducial System (OFS). These are mounted on an X-Y scanning system consisting of gimbals, flex pivots and actuators. The scanning system translates the X-ray beam across the sample surface to allow investigation of spatial variations in sample chemistry. PIXL's 100 μm -diameter X-ray beam can be scanned in 100 μm steps up to 25 mm along X and Y axes, while the co-

aligned OFS ensures visual registration of the XRF measurements as different parts of the sample are targeted.

X-ray assembly (XRA)

The XRA includes an X-ray tube, high voltage power supply, polycapillary optic, X-ray detector. The XRA performs the XRF chemical analyses by stimulating, and then measuring, sample fluorescence. This fluorescence is stimulated with an x-ray beam produced by a side window x-ray tube driven by a 28 kV high voltage power supply (HVPS). The X-ray tube (Figure 2), which has successfully passed an array of vibration, shock, thermal cycling tests, is a rhodium anode, grounded cathode design, produced by Moxtek, Inc (Orem, UT). X-rays are produced by the x-ray tube when the anode is struck by a micro-focused 20 μA electron beam. This x-ray beam is collected and then focused to a 100 μm spot by a polycapillary optic developed by XOS Inc. (Greenbush, NY). The polycapillary optic is a monolithic structure consisting of millions of glass capillaries. The capillaries are formed such that grazing incidence forms a tight, well-defined x-ray focal spot without significant lobe structure. The x-ray tube anode is held at +28kV by a novel HVPS. This miniature power supply, designed by Battel Engineering, will be fabricated by the University of Michigan's Space Physics Research Laboratory.



Figure 2 – The PIXL X-ray tube is a rhodium anode, grounded cathode design and has passed vibration, shock and thermal cycling tests.

The XRA has two key challenges. One is to maintain electric field confinement in the ~ 8 torr Martian atmosphere. The Martian surface environment is unfavorable for high voltage electronics, as the nominal surface atmospheric pressure corresponds to the lowest breakdown voltage across a gap, i.e. the minimum breakdown voltage described by the Paschen curve. As a result the integrity of the electrical insulation is critical. The second key challenge for the XRA also relates to the Martian environment, which has a typical diurnal variation of $\sim 100^\circ\text{C}$ and can reach temperatures as cold as -128°C . The extreme cold temperatures and extremely large diurnal variation place severe demands on

instrument thermal design and materials selection. For PIXL, the extreme temperature swings and the tenuous atmosphere combine to make the design of the high voltage portions of the instrument particularly challenging.

The spectrum of the fluoresced X-rays is measured by a silicon drift detector (SDD). The FAST SDD (Amptek Inc., Bedford, MA) used in PIXL incorporates a CMOS preamplifier to enable the energy of the emitted x-ray photons to be measured very precisely (125 eV FWHM), even at the very high flux rate produced by the focused X-ray source.

Optical Fiducial System (OFS)

To ensure the measured chemistry is unambiguously tied to the textural features in the targets, PIXL has an optical fiducial system (OFS) co-aligned with the X-ray beam (Figure 3). The OFS consists of a color micro-context camera, flood illuminator, and an LED illuminator that projects a reference grid onto the target. Together these are used to acquire visible images of the sample and enable visual registration of the position of the X-ray. The Micro-Context Camera has spatial resolution of 50 μm per pixel and a field of view of 29 x 36mm. This allows observation of textural features and microstructures as small as PIXL's X-ray beam, across an area of similar size to an abraded patch produced by a surface preparation tool on the rover.

While an image is being taken, an array of light spots will be projected onto the sample surface. The spot array has a fixed geometric relationship to the X-ray beam, to provide a means of spatially correlating measured chemistry to observed visual features. During operations, the amount of imaging required will vary depending on the PIXL measurement strategy being used. In the case of high resolution grid maps, there is typically enough information in the map itself to allow correlation with visible images - grain boundaries and other features become apparent in the chemical map. But when analytical spots are more widely spaced, a separate means of position verification is needed and the OFS would likely be used for every spot.

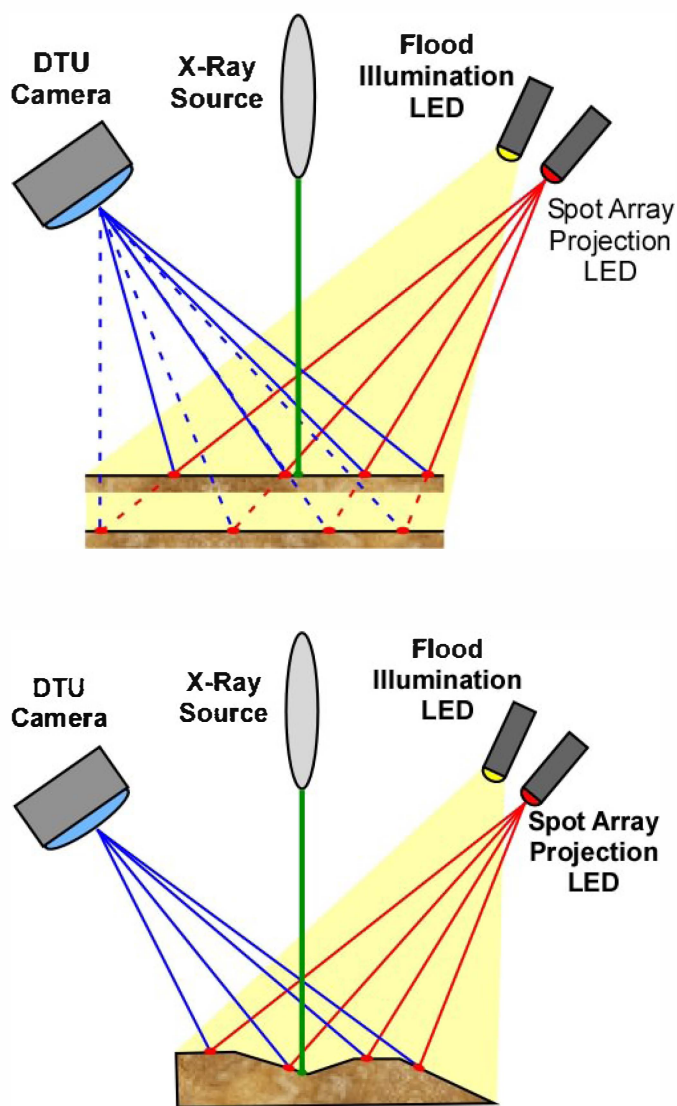


Figure 3 – The PIXL Optical Fiducial System (OFS). Changes in the geometry of the light spot array on the sample surface enable determination of the source-sample distance and the location of the X-ray spot.

Requirements on the Rover System

PIXL micro-XRF does not require a smooth, highly polished surface because the X-ray beam is relatively columnar so that the spot size does not vary significantly with distance from the focal plane. As a result, PIXL can tolerate millimeter-scale target roughness (on-par with roughness of surfaces that might be produced by a rover-mounted abrasion tool). Several millimeters of topographic relief can be tolerated with little or no effect on the overall quality of geochemical data or images.

PIXL relies on the flight system to place the instrument head within a short distance ($\sim 2\text{cm}$) of the target. If the distance is larger, the X-ray beam diameter increases, resulting in reduced spatial resolution. For example, at $\sim 2.5\text{cm}$, the beam diameter increases from 100 μm to 500 μm approximately. Thus, several millimeters of Z variation

can be tolerated while retaining sub-millimeter spatial resolution. Calculations of absolute abundance would also be affected by variations in Z. However, it is possible to correct for distances up to 4 cm using variation in the scattered Bremsstrahlung to infer Z distance [3] or by using the optical fiducial system to calculate Z distance.

4. PIXL PROTOTYPE

The PIXL breadboard instrument (Figure 1) incorporates the key design elements of the PIXL flight model, but uses commercial components. A Moxtek high-voltage power supply (HVPS) and X-ray tube are aligned and mated to an XOS polycapillary optic. The optic produces an X-ray beam with a 100- μm full-width-at-half-maximum (FWHM) focal spot at 2 cm from the optic tip. An Amptek FAST detector measures the fluoresced X-ray spectrum with 125 eV energy resolution and single photon sensitivity. A focused light beam is aligned with the X-ray beam on the sample surface and a CCD camera images the sample surface to provide position knowledge. Mechanical translation stages control x-y rastering of the X-ray beam.

The breadboard instrument has been used for over 5,000 hours of data collection while analyzing a wide variety of natural rock samples, minerals, powders and certified reference materials under various operating conditions. This extensive experimentation enabled the PIXL team to characterize the instrument, refine component properties (e.g., anode material) and operating parameters (e.g., voltage, current) and establish performance. After analyzing many hundreds of samples, it was determined that a Rh anode and 20-30 μA current in combination with 28 keV and the FAST version of the Amptek Silicon Drift Detector (SDD) enabled confident detection of geologically important elements down to trace levels while minimizing power consumption and integration time. The breadboard PIXL instrument was also used to establish the key performance parameters, as described below.

Instrument Performance

PIXL's X-ray beam is 100- μm -diameter, resulting in the ability to resolve the chemistry of submillimeter-scale features in natural geologic samples. The high X-ray flux produced by PIXL's X-ray tube and focusing optic means PIXL can measure most major and minor elements at 0.5 wt% in five to ten seconds. Thus, in 10–20 min, PIXL acquires excellent spectra on up to a hundred different spots on a sample, and during longer (e.g., overnight) experiments, PIXL can produce detailed element maps comprising thousands of individual spectra. Multiple spots can be summed for bulk analysis.

To detect most trace elements with PIXL generally takes 30 s to 2 min. The time taken to detect a given trace element is influenced by matrix effects as well as the abundance of the element itself. PIXL can detect most trace elements at very low concentrations (to 10's of ppm). These low detection limits were established through analysis of standards and

dilution experiments on the PIXL breadboard, although for many elements the detection limit may be better than indicated, as PIXL's lowest detection limit was not measured due to the lack of low-abundance standards.

PIXL's high sensitivity is enabled by high X-ray flux, and the multiplicative effect of small spot size. For example, one 100- μm schreibersite grain in a 2-cm field of view (FOV) would contribute less than 5 ppm Ni to a bulk measurement, and hence be undetectable, whereas the concentration under PIXL's beam would be 22 wt% (~40,000 times greater).

PIXL can detect a broad suite of elements—in addition to the 16 elements routinely reported by the APXS instrument on MSL, PIXL can detect: V, Co, Cu, Ga, As, Rb, Sr, Y, Zr and Ce (e.g., Figure 4). PIXL would also detect the levels of Ge that APXS has reported at Yellowknife Bay on Mars (McLennan et al. 2013). Many of these trace elements have important affinities in sediments, especially for clays and organic materials, and ratios such as Rb/Sr, Sr/Ca, and Ce/Y are widely used to determine petrogenesis in magmatic evolution and provenance in clastic sediments.

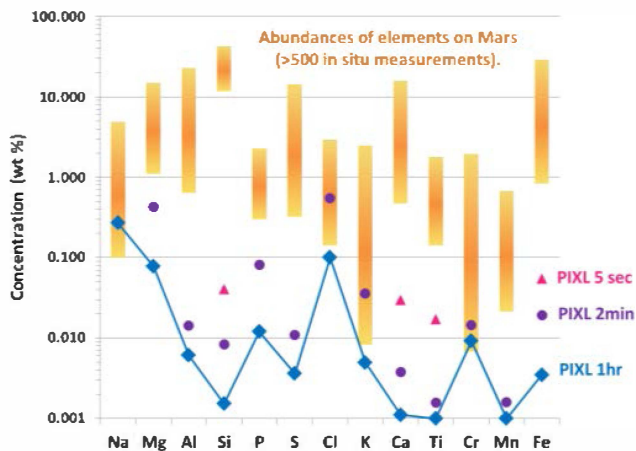


Figure 4 -

Detection of this wide array of elements is aided by PIXL's rhodium target and operating voltage, emitting both K and L lines in addition to the broad continuum, which maximize trace element detection while also maintaining excellent sensitivity to light elements (Na, Mg, Al, Si). Using the ratio of Rayleigh- and Compton-scattered Rh K lines, it would also be possible to estimate abundances of light elements (e.g., C, H,N,O) that are present in a target but not detected directly with XRF [4].

The PIQUANT calibration and data reduction software was created for PIXL, tailored from an extensive existing collection of spectrum processing and Fundamental Parameters XRF analysis codes developed for the Mars Borehole XRF Spectrometer [3]. PIQUANT has been successfully used to establish the accuracy of the PIXL breadboard. The quantitative analysis of measured spectra using the PIXL breadboard instrument follows the fundamental parameters method [5] with some

enhancements and modifications. This method was used with excellent results for the Viking XRFS instrument. Atomic data for the intensity calculations was taken from the database by Elam [6]. Rather than cast the measured and calculated intensities as relative to pure elements, as described in [5], absolute intensities are calculated. The calculated intensities include additional secondary effects such as fluorescence cascade. The X-ray tube spectrum is generated via the prescription recommended by Ebel [7] and the spectral transmission of the polycapillary optic was obtained from the manufacturer.

5. IN SITU OPERATIONS

During operations, PIXL would be deployed by the rover arm and placed ~2cm from the rock surface. The 2 cm standoff distance would be achieved with the aid of a contact switch. Once the appropriate position is attained, PIXL would begin its measurement.

PIXL has four measurement modes to suit target characteristics and available resources (Figure 5): a coarse prospecting mode (Strategy 1), line scanning (Strategy 2) or grid (Strategy 3) modes with varying coverage and density and short dwell times, and a long dwell point analysis mode (Strategy 4) for maximum sensitivity. The choice of strategy would be made on the basis of visible images of the rock taken by cameras on the rover (engineering camera, mast camera or arm-mounted camera may all be suitable). If the rock has not been abraded, strategy 1 or 2 is most appropriate. If the rock has been abraded to a flat surface, strategy 3 may be desired. Strategy 4 would likely only be used as a secondary analysis, when features of particular interest are noted in the first measurement and a follow-up measurement is planned, for example with increased dwell time to improve trace element quantification.

Note that while Strategies 2 and 3 rely on short dwell times, PIXL employs “Adaptive Sampling” to ensure at least one long integration for each different rock component encountered in an experiment. Adaptive Sampling uses a simple algorithm to assess incoming spectra and recognize major changes in composition. When a significant enough change occurs, a long dwell is triggered to ensure trace elements are measured at least once in every major component of the sample. PIXL’s array of measurement modes is carefully designed to fully utilize PIXL’s capabilities while adapting to science opportunity and operational constraints.

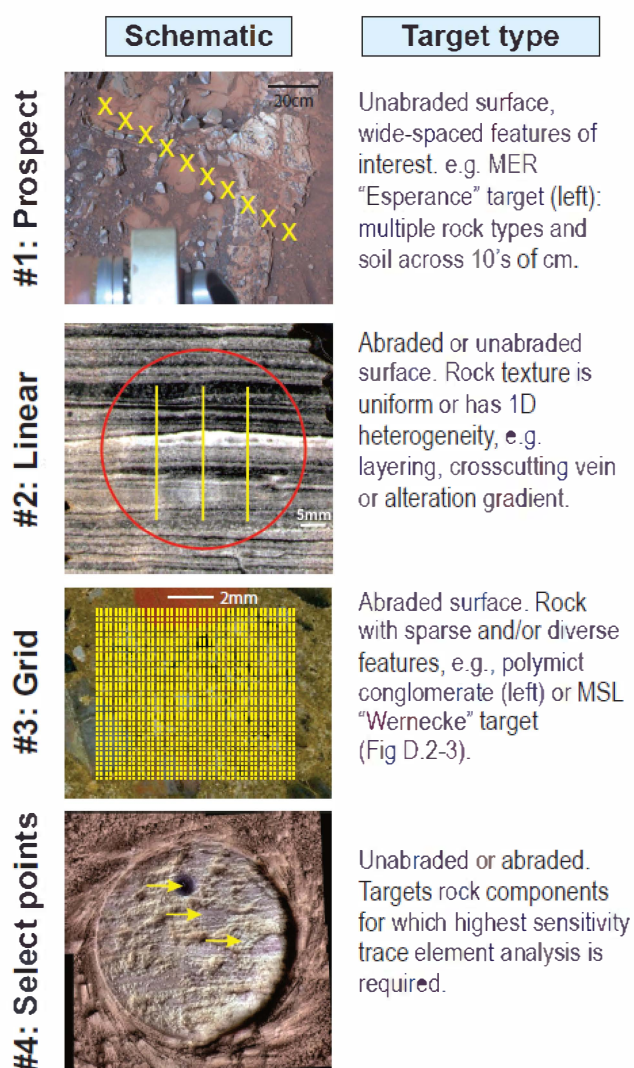


Figure 5 - PIXL’s measurement modes.

6. PIXL ANALYSIS OF PALEOARCHEAN CONGLOMERATE

The Paleoproterozoic conglomerate sample is a good test case for PIXL analysis because it is very heterogeneous, with several different types of grains, layers, veins and matrices. Understanding the chemistry of those different features provides insight to the formation and origin of the rock. The sample is significant because it contains an unconformity – a surface that was exposed and eroded subaerially in the past. The rock above the unconformity belongs to the 3.45-3.35 billion-yr-old (Ga) Strelley Pool Formation, whereas the rocks below belong to an older unit, possibly Duffer Formation (3.46 Ga). The erosion surface between them is the oldest unconformity in Earth’s geologic record. Deposits associated with unconformities are significant because they can provide insight to the ancient surface environment, including the atmospheric composition.

The PIXL breadboard was used to map the sample chemistry over an area 1x2 cm in size. The X-ray beam was

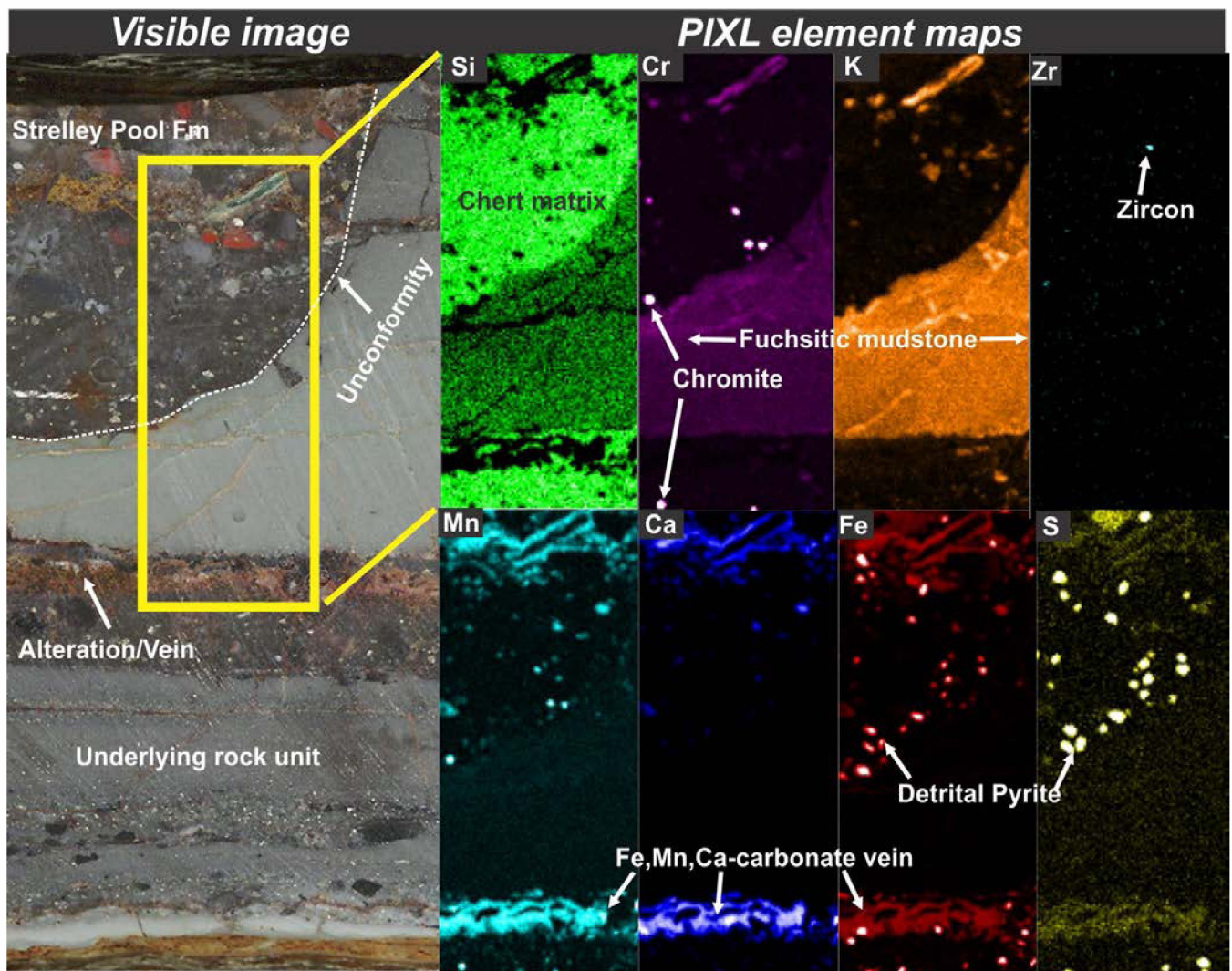


Figure 6 - PIXL element maps reveal spatial correlations between elements (constraining mineralogy), and between composition and texture, (constraining the origin and significance of the rock and its components). These maps show a 3.45 Ga silicified, fuchsite-(Cr-bearing clay) mudstone-conglomerate with detrital chert, basalt, jasper, pyrite, zircon and chromite and Fe, Ca, Mn - carbonate. Carbonate resides in a zone of alteration, which greatly reduces its significance for habitability. Detrital pyrite and pervasive silicification have positive implications for preservation of organic biosignatures. Height x Width of mapped area = 2x1 cm.

moved in 100mm steps, with 10 second integration at each

spot. The resulting spectral dataset was used to create the element maps shown in Figure 6.

These maps show different groupings of elements associated with the different geologic features. The element groupings provide insight to the minerals present. The fine grey-green mudstone layer has higher concentrations of Si, Al, K and Cr: this layer is a silicified, mudstone containing fuchsite (Cr-bearing clay). PIXL highlights the diverse compositions of clasts within the rock, including: chert, basalt, jasper, pyrite, zircon and chromite. An irregular brownish vein crossing the sample is a carbonate containing Fe, Ca, Mn. Grains enriched in F and S are pyrite mineral grains. The presence of detrital pyrite may indicate a reducing atmosphere at the time of deposition. Detrital pyrite and pervasive silicification have positive implications for preservation of organic biosignatures.

7. PIXL ANALYSIS OF PALEOARCHEAN STROMATOLITES

The Strelley Pool Formation (SPF) contains stromatolites: decimeter-scale, internally laminated conical and domical structures formed on the ancient seafloor. Similar structures in younger rocks and modern settings are commonly associated with microbial mat communities, and most ancient examples are thought to be biogenic. However, due to their extreme antiquity, the biogenicity of the SPF stromatolites was debated at length following their discovery [8]. A key question central to assessing the origin of the stromatolites, is whether the stromatolite layers were chemically precipitated crusts or layers of loose sediment stabilized by microbial mats. In the domical stromatolites, the layers have an irregular character with local features resembling “fenestrae” (former voids in the sediment, often associated with microbial mats, where gases produced in the mat create voids in the sediment). This fabric suggests the stromatolites formed by accumulation of loose sediment with microbial mats, rather than by chemical precipitation. However, an alternative hypothesis is that the carbonate mineral assemblage and textural properties are the result of burial alteration processes, and cannot be used to infer anything about the original sedimentary environment or processes. Allwood et al. [9] used micro-XRF to examine textural and compositional variations across the different types of stromatolites. The PIXL maps of calcium and iron highlight multiple phases of dolomite (a carbonate mineral containing varying amounts of Fe, Mg, Ca) differentiated by Fe-content. A higher-Fe dolomite forms a layer around the outside of the putative fenestrae, which indicates formation of a cavity-lining cement in the near-subsurface as sedimentary pore waters evolved. The recognition of these fenestral cavities also attests to the primary sedimentary origin of the carbonate minerals, which in turn allows paleobiologists to attribute the geochemical and textural characteristics of the carbonate to primary processes (rather than post-sedimentary alteration processes). Thus, PIXL’s texture-specific element mapping provides key evidence for biogenicity of the SPF stromatolites.

8. PIXL ANALYSIS OF NEOARCHEAN STROMATOLITES

Tumbiana Formation stromatolites formed through microbe-sediment interactions on a lake floor ~2.7 billion years ago. They have been well-studied [10, 11, 12], but the mechanism for stromatolite accretion is not well understood. For example, it is not clear whether the carbonate comprising the stromatolites was precipitated at the sediment-water interface, or instead represents fine carbonate particles that settled from suspension and were later incorporated into the stromatolites through microbial trapping and binding. In addition to distinguishing between modes of accretion, the detection of detrital grains in conical stromatolites offers an effective test for biogenicity, since a microbial mat must be present in order to adhere detrital grains to steep-sided features. Conventional methods such as optical microscopy are not well-suited to detecting detrital grains in these stromatolites, which consist of uniformly-sized and recrystallized carbonate crystals, and require the preparation of thin sections and time consuming searches across large areas. Bulk XRD analyses are also uninformative in that they have low spatial resolution and generally detect only calcite, silica and minor clay minerals.

Trace elements incorporated into carbonate rocks offer an additional way to distinguish between carbonate derived from different sources, and have been used in several studies to investigate the origins of ancient stromatolites [e.g.13, 14, 15] used destructive ICP-MS trace element analyses to distinguish between trapping and binding and *in situ* precipitation as modes of accretion of ancient stromatolites. PIXL was able to perform a similar task using non-destructive, micro-XRF based, rapid detection of Al, K, P, Mg, Mn, S and Zr concentrated in detrital grains, and Mg, Mn, S and Sr in carbonate during scans that could be performed in a field setting.

A 13 x 13 mm PIXL grid scan was acquired over the cut face of a slab prepared from stromatolites collected in the field (Figure 7). The X-ray beam was scanned in 100 μ m steps, with a 10 second integration at each spot. A line scan was made adjacent to the mapped area. The integration time for each spot in the line scan was increased to 2 minutes, to increase the sensitivity to trace elements.

A series of element maps were produced from the 13 x 13 mm grid scan dataset, revealing compositional variations across the sample (Figure 7). The Ca, Si, Fe, K, P, Mn and Ti maps highlight compositional differences between similarly-sized particles of carbonate (micrite) in the sediment deposited between the stromatolites and within the stromatolites themselves. Very fine grained clay minerals transported from elsewhere have contributed to the elevated K, P and Ti concentrations in sediments deposited adjacent to the stromatolites. Within the stromatolite, layers richer in K, P and Ti reflect periods when the incorporation of detrital sediments was relatively more important to stromatolite

growth. The results imply two different sources of carbonate, and suggest most of the carbonate in the stromatolites was precipitated *in situ*. Variations in the concentration of Ca, Fe and Si clearly delineate zones of post-depositional alteration of the stromatolite. This information is useful for reconstructing the diagenetic history of the rock and when undertaking analyses of carbonate that are aimed at reconstructing paleoenvironments, for example microdrilling for stable C and O isotope analyses, during which areas of more altered carbonate should be avoided.

The line scan increased PIXL's sensitivity to trace elements without imposing the time costs associated with raster mapping. Additional elements detected during the line scan include Al, S, Sr, and Zr. S and Sr identify and provide insights into the origins of different zones of carbonate and detrital material. Zr-spots in the line scan represent microscopic zircon grains which can be extracted and used for radioisotopic dating techniques.

The scale of the stromatolite layering and the associated compositional zonation identified by PIXL occur at a scale that is ideally suited to PIXL measurements.

9. SUMMARY

PIXL represents a significant advance in the ability to measure elemental chemistry of rocks and soils *in situ* on planetary surface missions. Taking advantage of recent advances in X-ray focusing optics and miniature microfocus

X-ray tube technology, PIXL would be able to measure the chemistry of individual sand grains. Because the tiny X-ray spot also has very high flux and hence rapid spectral acquisition, PIXL would be able to take thousands of spectra across a target during an experiment. The resulting chemical maps should reveal texture-specific chemical variations that enable detailed insights to past environmental conditions and processes, including habitability and potential for biosignature preservation.

There are unique challenges involved in preparing a PIXL instrument for flight, particularly the development of a 28 kV power supply for operation on the rover's robotic arm. However, the instrument design is straightforward and scientifically robust.

A prototype PIXL instrument at JPL has been used successfully for thousands of hours, and has demonstrated outstanding scientific performance. This prototype instrument has already contributed significantly to terrestrial research on problems relevant to Mars astrobiology.

10. ACKNOWLEDGEMENT

The research was carried out at the Jet Propulsion Laboratory, California Institute of Technology, under a contract with the National Aeronautics and Space Administration

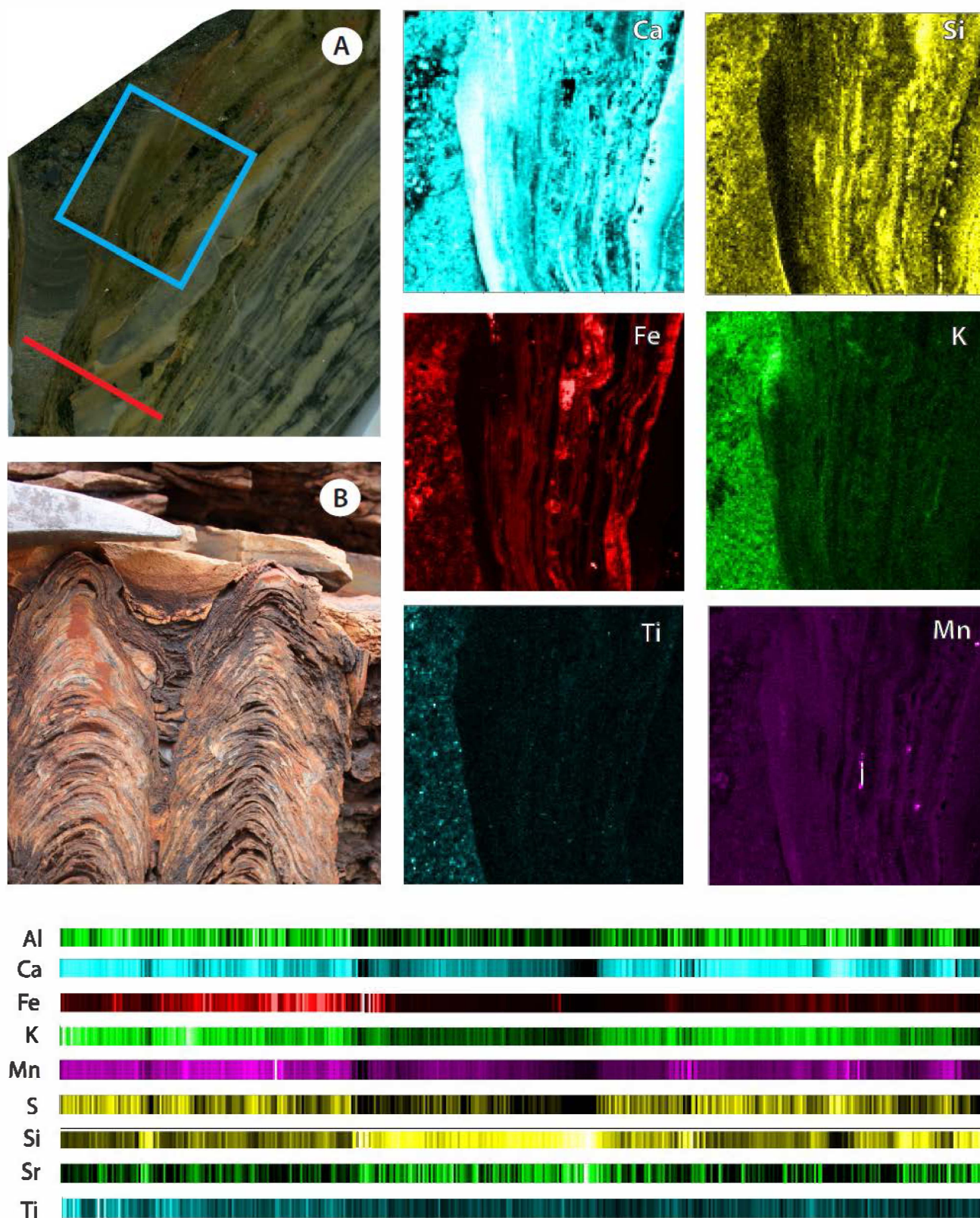


Figure 7 – PIXL element maps and a line scan made on a cut slab (A) of a Neoproterozoic stromatolite collected from outcrop (B) in Western Australia. The blue square delineates the area mapped by PIXL. The red line represents the path of the line scan. The sediments adjacent to the stromatolite are richer in elements associated with detrital input (Fe, K, Ti).

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BIOGRAPHY



Abigail Allwood is the Principal Investigator for PIXL, and a Research Scientist in the Planetary Science section at NASA's Jet Propulsion Laboratory. With a PhD in Earth Sciences from Australia's Macquarie University, Abigail's research focuses on ancient biosignatures and interpretation of past environments, using geological field methods and geochemical sample analyses. She first began using micro-XRF for her research in 2007.



Lawrence Wade is currently Instrument System Engineer for the Mars 2020 PIXL x-ray fluorescence spectrometer. He has developed instruments and tools for in-situ life detection on other planets and characterization of returned samples, including X-ray fluorescence, atomic force microscopes, super-resolution (<10 nm) optical microscopes for imaging biological samples in visible wavelengths, nanotube and dip pen nanolithography based protein patterning tools and microfluidic devices for characterized tissue DNA sequences. He is also Co-Investigator on both the Low Frequency and High Frequency Instruments on the European Space Agency's Planck Cosmic Microwave Anisotropy mission and Planck Scientist participating in instrument design and science data processing.



Ben Clark took the B.S. from the Univ. of Oklahoma in Physics, followed by graduate work at U.C. (Berkeley) and Columbia. His PhD is in biophysics and his main research areas of interest are planetary science, astrobiology and geochemistry. Ben developed the x-ray fluorescence soil analyzers for the Viking missions and also participated in the Phoenix mission's discovery of perchlorates on Mars. He is a science team member of the MER rovers and a Co-Investigator on the MSL "Curiosity" rover's ChemCam investigation, the OSIRIS-REx asteroid sample return mission, the Stardust NExT mission and the PIXL 2020 project. For 37 years he was with Lockheed Martin in Littleton, Colorado, serving as Chief Scientist of Space Exploration Systems, which built the Magellan, MGS, Odyssey, and MRO spacecraft. He also headed a group developing PI-led mission concepts, including the Stardust, Genesis, Phoenix, Juno, GRAIL, MAVEN, and OSIRIS missions, as well as several proposed future missions.



Tim Elam's main research interest is X-ray spectroscopy. He has worked in the areas of X-ray absorption, emission, fluorescence, and non-resonant inelastic scattering. His present efforts focus on using X-ray fluorescence in difficult environments. He has built an X-ray fluorescence spectrometer

(XRFs) to measure heavy metal contaminants in soils and sediments that is directly pushed via cone penetrometry without drilling. His latest project was a borehole XRFs for use in the Mars Subsurface Access Program and it is now being adapted to make in-situ measurements of diffusion of stable isotopes of nuclear waste elements through native rock without radioactivity. Dr. Elam is also the hardware lead for the APL Ice Diver. He is Chair of the Denver X-ray Conference, serves on the Advisory Board for X-ray Spectrometry, and is a member of the International Center for Diffraction Data.



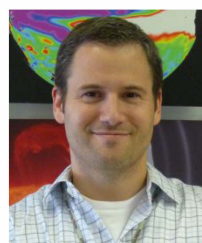
David Flannery is a geologist/astrobiologist with experience in the areas of field mapping, paleontology, sedimentology and stratigraphy. His primary research focus has been the stratigraphy, sedimentology, paleontology and geochemistry of Archean (2.5 to 4 billion-year-old)

geological formations in the Pilbara Craton, Western Australia. He is currently a Caltech Postdoctoral Scholar at the NASA Jet Propulsion Laboratory.



He has contributed to many aspects of flight instrument development and operation. He led the development of high-performance uncooled thermopile detector arrays from concept to flight build and delivery. These arrays are flying

on the Mars Climate Sounder (Mars Reconnaissance Orbiter) and Diviner (Lunar Reconnaissance Orbiter) instruments. For the Diviner instrument, he served as instrument system engineer, led the calibration effort, and participated in operations and data analysis.



Joel Hurowitz is an Associate Professor at Stony Brook University, and the Deputy PI for PIXL. His research interests deal with understanding the origin and evolution of martian soils and sedimentary rocks by exploring the relevant fluid-rock reactions which

control the alteration of primary igneous mineral phases and the formation of secondary minerals on Mars, exploring the causes of mineral surface reactivity in planetary settings in order to understand the enigmatic reactivity of Martian soil samples analyzed by the Viking landers, and the potential toxicity of reactive planetary soils to humans making extended visits to the surfaces of the Moon and Mars. Joel has also worked extensively on the Mars Exploration Rover mission as a member of the Athena science team.



Robert Hodyss is a Research Scientist at NASA's Jet Propulsion Laboratory. With a PhD in Physical Chemistry from Caltech, Robert has worked on science research and instrumentation for diverse solar system targets.

Robert is a Co-Investigator on the PIXL flight instrument project.



Emily Knowles is an astrobiologist with experience using synchrotron-based X-ray techniques to analyze geological materials. With a PhD in Geological Sciences from University of Colorado, Boulder, she has used a variety of X-ray and other spectroscopic techniques to

analyze ancient and modern biosignatures. Dr Knowles worked on the PIXL breadboard to help establish science performance