

MICRO-XRF: ELEMENTAL ANALYSIS FOR *IN SITU* GEOLOGY AND ASTROBIOLOGY EXPLORATION. Abigail Allwood¹ and Robert Hodyss¹, Lawrence Wade¹, ¹Jet Propulsion Laboratory, California Institute of Technology, 4800 Oak Grove Dr, Pasadena, CA, USA. Abigail.C.Allwood@jpl.nasa.gov

Introduction: The ability to make close-up measurements of rock chemistry is one of the most fundamental tools for astrobiological exploration of Mars and other rocky bodies of the solar system. When conducting surface-based exploration, lithochemical measurements provide critical data that enable interpretation of the local geology, which in turn is vital for determining habitability and searching for evidence of life. The value of lithochemical measurements for geological interpretations has been repeatedly demonstrated with virtually every landed Mars mission over the past four decades.

However, the current generation of flight instruments is limited in terms of ability to resolve the composition of small scale features and textures in the rocks, which is critical for detailed geological and astrobiological interpretations. At present, elemental chemistry measurements involve either spatially homogenized bulk elemental data across a 17mm diameter circle (APXS on Mars Science Laboratory) or single spot analyses from a mast-mounted camera meters from the target (ChemCam on Mars Science Laboratory). While these instruments provide valuable data, they are limited in their capacity to provide information about the relationship of rock composition to small scale textures, fabrics and structures. Understanding these relationships is crucial for resolving many critical planetary science questions, particularly those involving the search for, and analysis of, microbial biosignatures. If Mars science is to address such questions of astrobiological interest, more sophisticated investigations using detailed, spatially resolved *in situ* measurements are required.

On Earth, new lightweight, compact technologies enable high spatial resolution analysis of elemental chemistry using X-ray fluorescence (XRF). A key technical advance is the development of capillary optics that allow X-rays to be focused down to a narrow beam, which can be used to perform highly localized XRF measurements of elemental chemistry. Some instruments scan the beam across a sample to produce maps of element distribution at millimeter to centimeter scales. The technology required to produce results is inherently compact, lightweight and robust, which begs the question: can this revolutionary capability be developed for use on landed planetary missions?

Here we present initial results from a miniaturized micro-focus XRF breadboard instrument that we developed for potential flight on future rover or lander

missions. Significantly, the first results from the breadboard demonstrate that this instrument is capable of determining the elemental composition of rocks (elements Na-U) with sub-millimeter spatial resolution, and can acquire spectra in a few seconds to two minutes (compared to 15 mins to >2hrs for APXS). The advantages of this high spatial resolution and fast acquisition are (1) the ability to analyze the chemistry of small features such as individual grains and laminations, and (2) the ability to perform a large number of geological analyses within a relatively short time. Both of these capabilities would lead to a far more detailed understanding of local geology than possible with existing flight instruments. This level of knowledge is crucial for determining where biosignatures are most likely to occur and for acquiring the necessary contextual information to interpret any potential biosignatures that are detected.

Instrument description: Multiple breadboard instruments have been built over the past two years, to explore science and engineering trades. The final version of the breadboard instrument incorporates a novel, tightly focused x-ray tube and high voltage power supply (HVPS) developed by Moxtek Inc. that provides up to 200 μ A at 10 to 50 keV. The anode material is Ag. This x-ray tube was integrated with a custom polycapillary optic developed by XOS Inc. and then integrated with optical camera, fiducial laser and Amptek x-ray detector to form the breadboard Micro-XRF shown in Figure 1. The total mass of the complete breadboard instrument is only 2.76 kg including mounting hardware, mounting plate, shielding, camera, laser, etc.

The mass of the breadboard x-ray source is ~500g including the high voltage power supply. Most of that mass is brass shielding of the source, which is part of the commercial packaging for human shielding and unnecessary for flight. The x-ray tube anode focal spot demonstrated an elliptical cross-section with a full width half maximum (FWHM) minor axis width of 65 microns and a major axis width of 120 microns. Moxtek anticipates significantly reducing the ellipticity of the anode spot with further development.

The breadboard includes an Amptek Silicon Drift Detector (SDD) that draws 2.5 watts and has a resolution of 135 to 155 eV FWHM at 5.9 keV. It weighs 180 g including the preamplifier, digital pulse processor, multichannel analyzer, the detector and preamp power supplies, and packaging. The Amptek detector

has substantial flight heritage and was part of several flight versions of the APXS instrument (including those flown on Pathfinder, MER and MSL).

Rock samples are positioned relative to the instrument by a three-axis arm whose position is controlled by closed-loop translators (mimicking the movement of the robotic arm of a rover relative to the rock). The distance from the source to the detector is calculated from the position of a focused laser beam on the sample as imaged by a camera. Using this system we achieved better than 50 micron accuracy in measuring the distance from the x-ray source to the sample surface.



Figure 1: Two views of a breadboard micro-XRF. The size of the assembly can be seen by the optical table holes (1" centers). This instrument, mounted on a 3-axis control arm, was used to acquire the data presented here.

Sample analyses: Standards and natural rock samples were analyzed to test the breadboard instrument performance. USGS basalt glass standards BIR-1G and BHVO-2G were analyzed to evaluate the instrument's speed and detection sensitivity. The major elemental components (Si, Al, Ca, Fe, S, K, Mn etc) were detected in just one second. With longer integration times of 30-300 seconds the instrument was able to detect heavier trace elements, such as Zr, Sr, Ni and Cu, present at ~100 ppm (Fig 2). Note that figure 2 shows raw data: no processing such as continuum removal, tube line removal, or escape peak removal was performed. The fluoresced signal was substantially absorbed by air and therefore the detected signal is significantly less than would be observed in vacuum or in a martian atmosphere. With more sophisticated processing of data collected under vacuum, it is expected that confident detection of trace elements to 10 ppm will be achieved.

A suite of rock samples was also analyzed to assess the instrument's ability to differentiate the composition of small geological features (Fig 2-4). The samples included a 3.4 billion yr-old dolomite-chert stromatolite with 1-3mm laminae, and an altered tuffaceous mudstone-sandstone with clasts, veins and beds from ~2 to ~12mm. If rocks such as these were encountered

on another planet, the composition of these small scale features would need to be understood in order to properly interpret the rock—a bulk analysis alone would lead to ambiguous interpretation.

The samples were cut with a diamond saw to create a flat but slightly rough face akin to the abraded surface produced by a Rock Abrasion Tool or similar. On each sample, a linear transect survey was conducted on the cut face, with 1mm spacing between analyses along a 2-3cm line (beam diameter at each point ~100 microns). Acquisition time at each point was 120s. On each sample, spectra showed distinct variation as the beam traverse across the small visible features in the rock. The series of spectra from the stromatolite are shown in figure 2: at each of seven points the full spectrum is shown, revealing variations in elements present and their relative abundance. Results from the tuffaceous mudstone-sandstone are summarized in figure 3. At each point full spectra were acquired and analyzed—Figure 3 shows the along-transect variations in 6 of the elements detected. Along the path traversed, correlations between compositional variance and geological features were observed. For example, at point 15-19, an increase in Cr and Ti correspond to a layer of fuchsitic (Cr-bearing) tuff. An increase in Fe at point 2-3 corresponds with a jasper (hematitic) clast. Increases in Ca and Fe correlate with two orange-brown veins of iron carbonate mineral (around points 4 and 20-22). The entire rock is silicified, as seen in the fairly uniform levels of silicon along the transect (Fig 3). While further work is required to quantify these compositions, these data are consistent with the known geology of the sample and show that the Micro-XRF can spatially distinguish the elemental composition of millimeter-scale geological features. Even without quantification, the spatial co-variation of elements—especially if spatially correlated with visual clues such as color or crystal habit—can provide constraints on mineralogy. In a sense, Micro-XRF performs a level of petrographic analysis.

Science operation of a flight instrument: Three general modes of use are possible:

1. Single spot, long acquisition time (1-3 minutes) for semi-quantitative analysis of individual features. This would require precise positioning to ensure a particular feature is targeted.
2. Multi spot transect or grid with short to long acquisition time (few seconds to minutes). This mode (illustrated in the tuff example above) would not require precise targeting to commence the analysis and would serve as a triage or survey mode to identify most of the compositional features present. Spatial co-

variations in elements would aid mineralogical interpretations. At least one axis of translation would be provided by the instrument and some additional level of translation might be provided by the spacecraft robotic arm.

- 2D Raster map with short acquisition times and closely spaced spots. This mode would be designed to create a hyperspectral element map over a portion of the rock surface and would rely on two axis translation by the instrument.

Which of these modes is ultimately most important depends on trades between (e.g.) robot arm capability, data volume and instrument mass/volume. At a minimum, we envisage that with a single axis of translation provided by the instrument and no reliance on robot arm precision placement, the linear survey mode across an abraded patch of rock (e.g. like MER 3cm diameter RAT hole) would reveal the key components

of compositional variation in a rock and provide much more detailed petrologic insights than the bulk analysis of the whole surface area provided by current flight instruments.

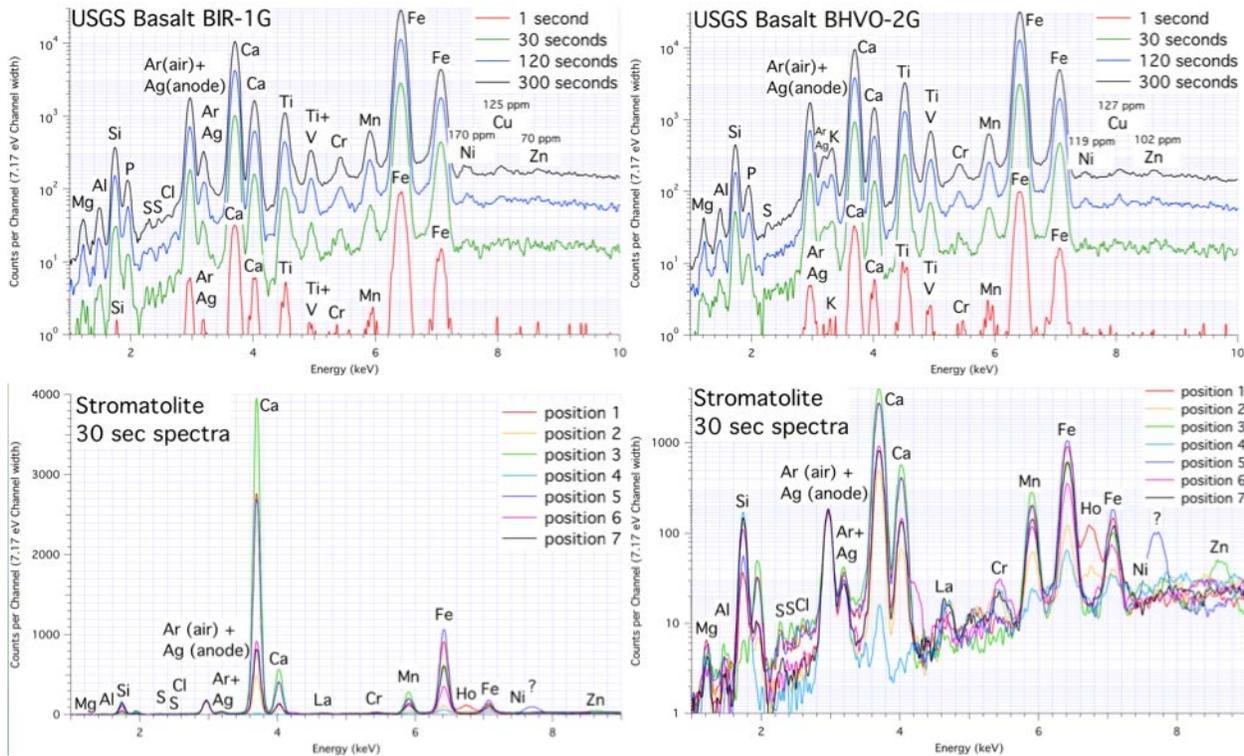


Figure 2. The upper panels are spectra of USGS Basalt glasses. The red spectra in these panels were acquired in 1 second. The green, blue and black traces were acquired in 30, 120 and 300 seconds respectively. Sensitivity to 100 ppm is readily achieved over these time scales. The optimal integration time in situ will vary between 30 s and 300 s with the content and morphology of the sample being studied.

The lower panels are linear and log plots of spectra acquired from a 3.4 billion yr-old stromatolite. Seven point (~100 μm) spectra were acquired along a line <3 mm long. The linear plot (3) clearly shows the elemental variation (and repeats) along this short line. The observed variation matches current geological understanding of the sample, revealing chert (SiO₂) and dolomite (CaCO₃) laminae, and variations in Fe and Mn content that distinguish primary and secondary dolomite phases. The log plot (lower right) demonstrates the sensitivity of a Micro-XRF to local elemental concentrations that would be totally lost in a spectrum taken over a large area. All of the spectra above were acquired in air using the polycapillary x-ray source operating at 28 keV and a filament current of 20 μA. The spectra shown were slightly smoothed but are nearly raw data. No processing to remove or compensate for the x-ray source background, escape peaks, diffraction peaks, air was done.

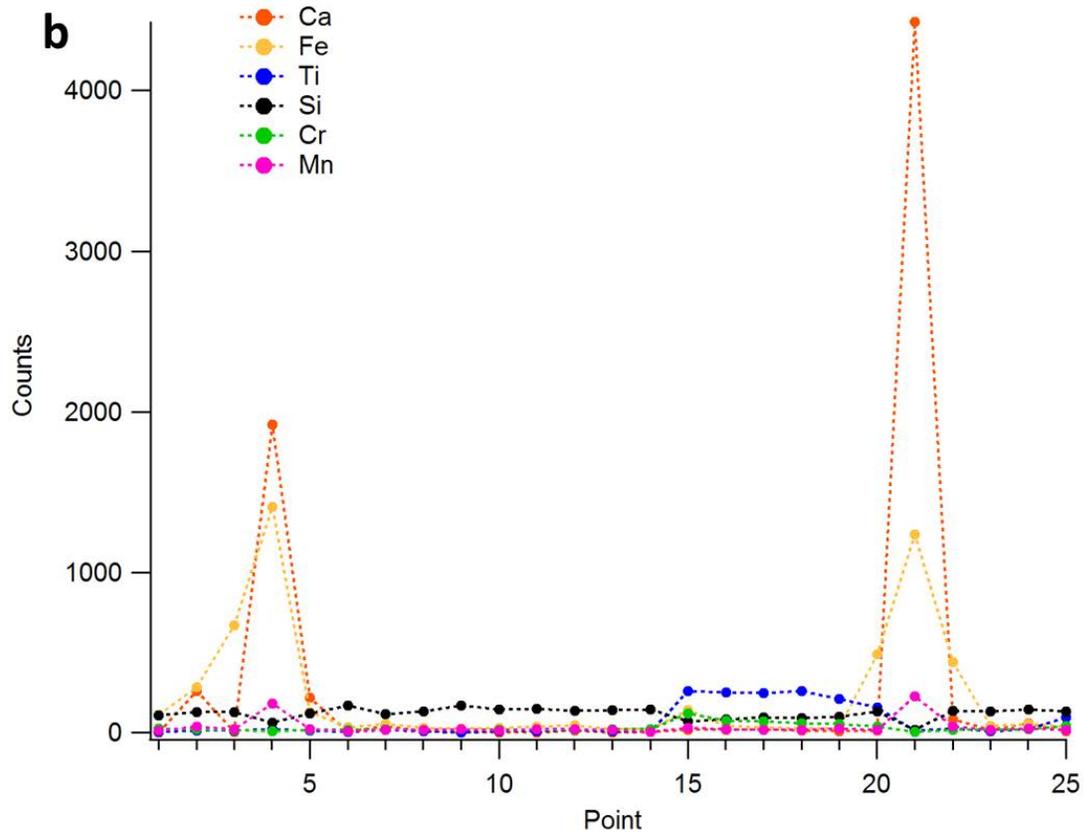
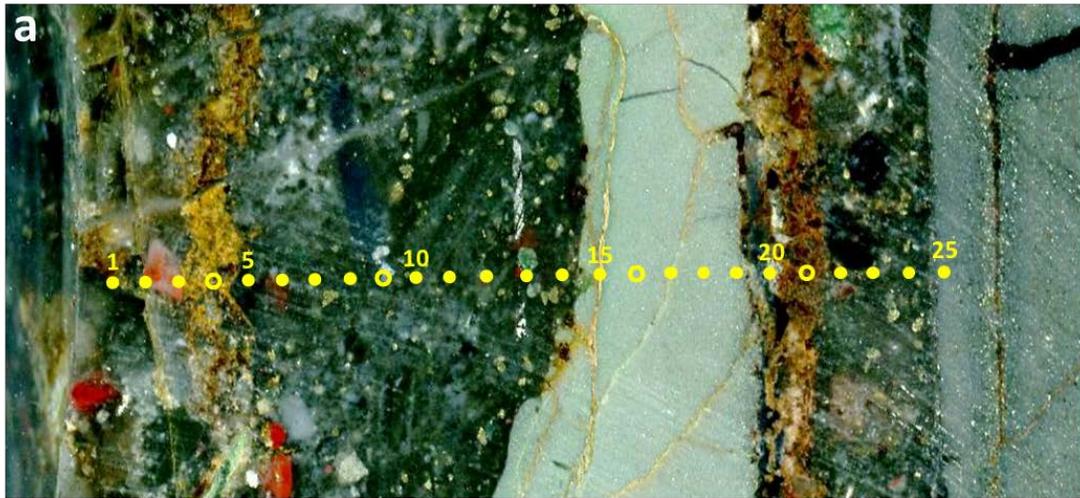


Figure 3. a) Photo of points sampled by the Micro-XRF breadboard system across an altered, thinly bedded tuffaceous mudstone-sandstone. Bedding is oriented vertically (paleo-up to the left). The spots represent the location of the x-ray beam at each analysis and are at 1mm spacings. b) Counts per channel for selected elements at each of the points in (a) from left to right, showing elemental variations that can be visually correlated with features seen in the image.