DATA VISUALIZATION OF MIXED-PHASE IRON SAMPLES WITH THE PLANETARY INSTRUMENT FOR X-RAY LITHOCHEMISTRY (PIXL).
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Introduction: The chemical composition of sedimentary rocks has the potential to reveal information about their depositional environment, which is essential for understanding past climatic conditions on Earth and Mars. In particular, redox-sensitive elements such as iron and manganese can provide insight into aquatic processes and conditions and the role that volcanism and oxygenation play in defining those conditions. As these conditions are important for determining the habitability of a planetary body, investigations of the Martian surface have focused on chemical and mineralogical characterization of the sedimentary record [1, 2].

The Planetary Instrument for X-Ray Lithochemistry (PIXL) is a microfocus X-ray fluorescence spectrometer that will be delivered to the Martian surface as part of the Mars 2020 rover and is capable of measuring major and trace elemental composition at submillimeter scales. To accomplish this, X-rays are generated by a Rh-target X-ray tube operated at 28kV. Those X-rays are focused from the X-ray tube to the rock surfaces using a silica polycapillary optic. The energies and intensities of emitted fluorescent X-rays are counted using a pair of energy-dispersive silicon drift X-ray detectors. The small spot size of PIXL (100-150 µm in diameter) allows the elemental chemistry of small features in Martian rocks, such as single sand grains, veinlets, and crystals, to be measured with high precision. This high degree of spatial resolution distinguishes PIXL from previous XRF instruments on Mars, which were focused on bulk lithochemistry rather than small-scale chemical variation [3]; these small-scale variations have the potential to provide new insight into past Martian habitability and biosignature preservation.

Processing XRF data involves calibration and fitting of the measured X-ray histograms to produce a spectrum that yields information about the elemental composition of the spot from which each spectrum was collected. Measurements of major and minor elements by XRF are typically reported in weight percent (wt. %). Inferences regarding sample mineralogy can be made on the basis of these elemental abundances by converting them to wt. % of oxides via an assumed stoichiometry. For example, to determine the amount of silica (SiO_2) in a sample, the percent abundance of silicon is multiplied by the molecular mass of SiO_2 divided by the weight of Si. However, these mineralogical inferences are made complicated when more than one oxide of an element exists in a single sample. This
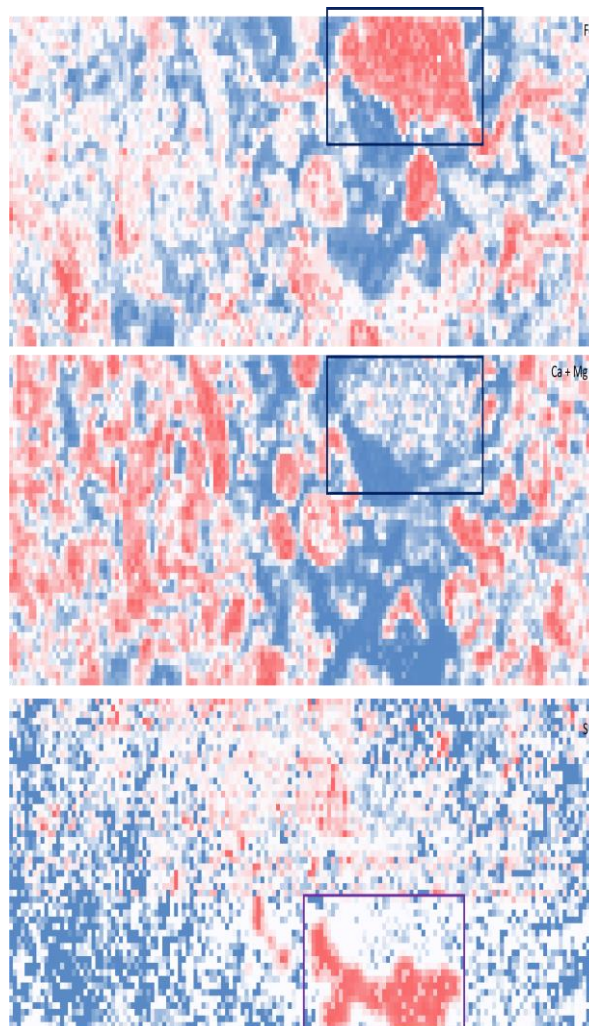

Figure 1. PIXL maps of sample PLBL107 (scan dimensions are 15x5 mm). (A) Map of Fe. (B) Map of Ca + Mg. (C) Map of S. Dark blue square represents a carbonate nodule; purple square represents a pyrite nodule.

is particularly problematic in iron-rich sedimentary rocks, such as banded iron formation, which often contain multiple oxides and can also be rich in Fe-carbonate and Fe-sulfides/sulfates [4]. In this study, we designed an algorithm using MATLAB that determines appropriate oxide or carbonate assignments for Mg, Ca, and Mn, and oxide, carbonate, or sulfide for Fe in samples that contain mixed mineralogical assemblages of these elements. The algorithm operates by iteratively selecting the set of compounds that brings the total abundance of all compounds in each individual spot

Figure 2. Example of an oxide/carbonate map of sample DRC-1. Blue represents SiO_2, light gray represents $CaCO_3$, dark gray represents $FeCO_3$, and green represents $MnCO_3$.

analysis as close to 100 wt. % as possible. A Microsoft Excel-based macro then takes these compound abundances and maps them in color-coded cells to produce compound abundance "heat maps" (**Fig. 1**) or maps of the most abundant compound in each individual X-ray spectrum (**Fig. 2**). In this way, it is possible to create maps of inferred compound and mineral abundance using PIXL XRF data, which can be ground-truthed against petrographic analysis by transmitted light microscopy.

Samples: Samples were selected from a well-characterized suite collected from the banded chert-carbonate facies of the Gunflint Iron Formation (described more fully in [*5*]). These samples contain the iron oxides hematite and magnetite, and are also abundant in siderite and ankerite [*4*]. An additional sample (DRC-1) was analyzed from the Zebra Locality of the Dresser Formation of Western Australia (provided by Martin van Kranendonk). Sample slabs were cut to a thickness ranging from millimeters to several centimeters using a diamond-coated, water-cooled tile saw (the range of thicknesses in the samples does not affect our measurements because all samples were thicker than the maximum X-ray penetration depth [*3*]).

Methods: Samples were measured using a bread-board version of the PIXL instrument located in the Geochemistry Lab of the Center for Planetary Exploration (CPEx) at Stony Brook University. For all measurements, the X-ray source was set to a voltage of 28kV and an amperage of 175μA. Scan dimensions ranged from single line scans of 15mm length to full map-size scans of 5x15mm. Areas of interest, such as veins, inclusions, and carbonate nodules were targeted in order to produce maps with maximum chemical variation. All scans were produced with a step size of 0.1mm and an integration time of 10s. Raw XRF measurements were converted to elemental abundances using the PIQUANT software package [*6*]. Typically, elements quantified in this step included Si, Ti, Al, Na, K, P, Ca, Mg, Fe, Mn, and S.

Results & Discussion: Examples of optimized maps are shown in **Figures 1 & 2**. The sample shown in **Figure 1** is PLBL107, which contains magnetite, hematite, Fe-Mg carbonate, and small pyrite inclusions. This map has dimensions of 15x5mm, and in that area it is possible to observe small-scale mineralogical variation that would not be seen if bulk chemistry alone was analyzed. Highlighted features include a siderite nodule that is Mg-rich and Ca-poor (**Figure 1A, 1B**) and a sulfur-rich concretion that is interpreted as diagenetic pyrite (**Figure 1C**).

Shown in **Figure 2** is a composite map of DRC-1, highlighting our ability to map the dominant inferred mineral phases in the scan area, in which an aragonite splay that has been diagenetically altered to Fe-rich carbonate is clearly seen. [*7*].

Initial evaluation indicates that mineralogical assignments by our MATLAB-based algorithm and Excel-macro-based maps closely mirror sample petrography. Future work will include more in-depth comparisons between our geochemical maps and transmitted light microscopic images. Understanding the challenges associated with identifying the mineralogy of complex samples is critical as preparations for Mars 2020 continue. The software developed in this project can improve data processing with the PIXL instrument, and thus the ability of the scientific community to interpret geochemical data returned during the Mars 2020 rover investigation of Jezero Crater and its surrounding region.

References: [1] Vaniman, D.T. *et al.* (2014) *Science, 343.6169:* 1243480. [2] Squyres, S.W. e*t al*. (2004) *Science, 306.5702:* 11709-11714. [3] Allwood, A. *et al*. (2015). [4] Floran, R.J. & J.J. Papike (1978) *Journal of Pet., 19.2,* 215-288. [5] Holme, E.A. *et al*. (2017). *LPSC XLIX* Abstract #2333. [6] Allwood, A. e*t al.* (2018) *Nature, 563.7730.* [7] Otalora, F. *et al.* (2018) *Journal of App. Cryst., 51.4*.