2016 CANMARS ANALOGUE MISSION: INSIGHTS INTO THE UTILITY OF X-RAY FLUORESCENCE SPECTROMETRY FOR THE IDENTIFICATION OF PALAEOENVIRONMENTS SUITABLE FOR ANCIENT BIOSIGNATURE PRESERVATION. S. L. Simpson[1], S. Duff[1], J. O'Callaghan[1], C. Caudill[1], G. R. Osinski[1,2]. [1]Centre for Planetary Science and Exploration / Dept. Earth Sciences, University of Western Ontario (ssimps56@uwo.ca), [2]Dept. Physics and Astronomy, University of Western Ontario, London, ON, Canada.

Introduction: The final operational cycle of CanMars, a high-fidelity Mars Sample Return analogue mission (MSR), was completed successfully in Fall 2016 [1]. In partnership with the Canadian Space Agency (CSA) and UK Space Agency (UKSA), the mission was operated by the Centre for Planetary Science and Exploration (CPSX) at the University of Western Ontario, London, Canada as part of the Natural Sciences and Engineering Research Council (NSERC) CREATE initiative titled "Technologies and Techniques for Space Exploration" (create.uwo.ca.). A suite of instruments integrated with the CSA Mars Exploration Science Rover (MESR), built by MacDonald, Dettweiler and Associates Ltd. (MDA) were deployed in order to fulfill the overall mission goals as follows [2]: (1) geologically characterize a concealed Mars analogue field site located in Utah, USA; (2) test CSA rover hardware and software for future missions; (3) vet operational, procedural, and sample acquisition workflows of a MSR mission; and (4) document operations and logistics necessary to carry out future high-fidelity analogue missions. During the 2015 mission cycle, the X-ray fluorescence (XRF) spectrometer was used as a stand-in instrument for the Mars2020 LIBS instrument, and thus mimicked remote observation capabilities up to 7 m from the rover location [3]. This instrument was very useful during the 2015 mission cycle due to the quantitative nature of the data and the remote capability [3], however, reliable geologic interpretation was necessarily accomplished by a suite of instrumentation. Information about grain size and morphology from high resolution/small field of view imagery and lower resolution context imagery were combined with a number of spectrometers to provide contextual interpretations of the field site.

Having previously characterized the main lithologic units and depositional environment of the field site during the 2015 mission cycle [1, 3, 4], the primary science goals for 2016 were to assess the potential of specific lithologies to preserve evidence for ancient life and directly detect biosignatures as organic carbon [2]; this was carried out using X-ray fluorescence (XRF), Raman [5] visible-infrared (VIS-IR) [6] and laser-induced breakdown (LIBS) spectrometers [7]. These were complemented by the micro-imagers TEMMI, Watson and RMI [8].

This report details (1) the 2016 pre-planned goal for XRF data acquisition and utility versus the actual role, as determined by data return throughout mission operations while in simulation; and (2) likely causes for errors encountered with the 2016 data return.

CanMars XRF: During the 2016 cycle, a handheld XRF spectrometer was used to emulate the Mars 2020 mission's PIXL contact XRF [9]. This is essentially a different test in operational usage of the XRF instrument from the 2015 mission cycle, which was benefited from mimicking remote observation capabilities. The pre-planned scientific goal for the instrument was to aide in the identification of lithologies conducive to the preservation of ancient biosignatures by providing geochemical information on the elemental abundances of a target, to be used in conjunction with the other spectral instruments. Specific mineral groups and lithologies sought out were sulfates, sulfides and carbonates, and anoxic iron-rich shales or sandstones [2]. A total of seven nine-point data rasters were obtained from seven individual targets that were determined to be sandstones, shales and clays, based on visual imagery. XRF data were obtained using a field portable handheld Bruker Tracer IV-SD energy dispersive XRF equipped with an Rh X-ray target with a maximum tube voltage of 40 kV, detector area of 10 mm^2, and typical resolution of 145 eV at 100,000 cps using a Silicon Drift Detector (SDD); each set of target analyses were run for a total of 60±1 seconds.

Results: XRF data return during field operations yielded poor results; of the 63 measurements obtained only 13 generated weight percent (wt%) totals of more than 50%, severely limiting the utility of XRF in meeting the 2016 scientific mission goals. The average wt% total for a single measurement was 36.9%, ranging from 8.82% (lowest) to 63.3% (highest); totals were slightly higher for sandstone targets. The major element yields that were generally within error limits are MgO, Al_2O_3, SiO_2, P_2O_5, K_2O, TiO2, MnO and Fe_2O_3. Trace elements (e.g. Ni, Cu, As) were sporadically detected, but often with very high errors.

Discussion: The utility of XRF measurements to mimic the Mars2020 PIXL instrument that were obtained in-simulation during the 2016 mission cycle was highly limited as evidenced by the poor data return. This is likely due to a combination of errors encountered during data acquisition. Furthermore,

assessing measurement uncertainty (average sampling variance, analytical variance, reliability) and confirming precision for quantitative data requires a robust dataset; the operational use as a contact instrument resulted in very few data points (as opposed to the much better data return from the 2015 mission cycle).

The depositional environment of the Mars analogue field site is characterized by gradational sequences of lacustrine, fluvial and possibly shallow marine sandstones, siltstones, mudstones, pebbly conglomerates and evaporite horizons [2]; multiple units are interspersed with layers of smectite clays, variety montmorillonite, as detected by the VIS-IR instrument [6], which is interpreted to have originated from volcanic ash fall deposits. The "popcorn" texture created by the shrinking and swelling of hydrated clay minerals was prevalent throughout the field site, and often completely concealed outcrops (Figure 1); this resulted in a thick clay crust that not only obscured underlying lithologies, but also created an uneven and pitted surface unsuitable for accurate contact spectral analysis. XRF analyses on very uneven surfaces can affect the contact angle between the beam and target; in cases where the beam was not perpendicular to the contact surface, the resulting data are likely less accurate.

Figure 1: Outcrop of green and red shales at the Utah Mars analogue field site, unearthed from the ubiquitous "popcorn"- textured clay crust created by the shrinking and swelling of smectites.

Elements where Z (atomic number) < 12 (or with x-ray energy < 1.254 keV) are below detection limits are not accounted for, which will also yield low totals. Additionally, carbonate minerals, if present, provide misleading XRF data; as an example, CaCO3 has 43% Ca and 57% CO3, which would yield erroneous, inaccurate readings of 100% Ca. In the event that an analysis has a very high concentration of one particular element, such as silica in Si-rich sandstones and tuffs found at the field site, an effect called "shielding" or spectral interference [10], in which the peak of an element masks those of adjacent elements in the spectra, may cause an underestimation of elements in the XRF software.

Conclusions: The 2016 CanMars XRF instrument data return did not meet the pre-planned mission goals of providing geochemical information on lithologies in order to aide in the selection of samples most likely to preserve evidence for ancient life. The poor totals are likely due to complications associated with XRF data acquisition at the field site resulting from highly uneven surfaces, limited detection capabilities and possibly spectral interference for lithologies rich in a single element (e.g. silica). It's possible these problems could be mitigated by using an abrasion tool on highly weathered targets pre-analysis. A rich data set is also necessary for quantitative data; in this operational test, it was shown the time and energy constraints of using a contact instrument substantially limited the usefulness of this instrument. Nevertheless, multiple samples were acquired from the field site that are presently being analyzed in order to determine the validity of the multiple spectral datasets (i.e. XRF, LIBS, Raman, VIS-IR), and ultimately confirm the success or failure of rover acquisition of samples most likely to meet the 2016 mission goals of preserving organic carbon.

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