IN SITU X-RAY DIFFRACTION (ISXRD) FOR EXPLORING MARS MINERALOGY AND GEOLOGY.

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Introduction: Minerals record the geological processes, impact history, paleoclimate, and habitability of planetary bodies. Thereby, to understand the evolution of Mars, we need to study its mineralogical record. Rover-based instruments have measured elemental information from the surface (such as the Alpha Particle X-ray Spectrometer (APXS) on the Mars Exploration Rovers (MER) [1], and Mars Science Laboratory (MSL) [2] [3]), but elemental composition alone does not provide a complete analysis of which minerals are specifically present. X-Ray Diffraction (XRD) is the primary technique to determine the mineralogy of geologic materials. An XRD is currently being used on Mars as part of the CheMin instrument on NASA's MSL rover [4]; however, a major limitation is that CheMin requires a fine-grained sample from scooping or drilling, and has limited context regarding the inter-relationships between the minerals in the rock. A Canadian Space Agency (CSA)-funded team from Western, Brock, and Guelph universities, along with Canadian companies PROTO and MDA are developing a concept for a miniaturized *in situ* contact XRD (ISXRD) which will be able to analyze minerals directly on the martian surface. As a part of this concept study we have assembled a set of martian analogue rocks and minerals common on the martian surface, and martian meteorites. We compare XRD results from current laboratory-based µXRD at Western University with results obtained using various candidate miniaturized X-ray components and geometries tested by PROTO. This will lay the foundation for an improved contact XRD instrument to be used in future exploration by rovers or manned missions.

Methods: We assembled a set of ~60 Mars-related samples for which XRD data was collected on a laboratory µXRD, and on a miniaturized ISXRD testbed, using a variety of component geometries for comparison.

Analogue samples. We investigated samples of minerals (silicates, oxides, sulfides, sulfates, carbonates, salts) and rock types (igneous, sedimentary, hydrothermal, impact) known to occur on Mars, as well as martian and other shocked meteorites.

Standards. Corundum and LaB_6 were used in both laboratories for comparison.

Laboratory microXRD. Lab-based µXRD was collected on a Bruker D8 Discover µXRD (θ-θ) [5], using Bragg-Brentano geometry, with the listed parameters:

Source: Co radiation (standard sealed tube)
Collimation: Gobel mirror parallel beam optics with 300 µm pinhole collimator
Beam size: nominal diameter of 300 µm
Detector: Vantec-500 2D detector (2048 channel)
Power: 35 kV/45 mA
Mode: Omega Scan or Coupled Scan (stationary)
Angular Range: 15° - 110° 2θ (2 frames)

Testbed miniaturized ISXRD. PROTO Manufacturing used the configuration(s) below:

Source(s): Co, Cu radiation (XRT-60, XRT-32)
Collimation: none
Divergence Slit: 0.7 mm
Beam size: line beam: 760 µm x 8 mm
Detector: Mythen2 R 1D/1K (640/1280 channel)
Power: 30 kV/20 mA
Mode: Step Scan (θ-2θ)
Angular Range: 10° - 120° 2θ

Mineral ID was done using the International Committee for Diffraction Data (ICDD) database. In some cases, mineral modal proportions were determined using Rietveld refinement [6].

Results: Results for selected martian analogues and a martian meteorite are reported below (Figs. 1-3):

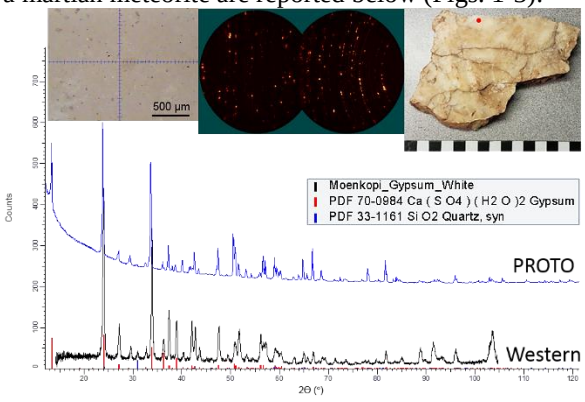

Figure 1: Comparison of lab (Western) and testbed (PROTO) XRD patterns for Moenkopi gypsum whole rock sample - excellent. Inset images are from the lab XRD at Western: L-R: target image; 2D XRD image; sample run at Western (black bar = 1 cm).

Terrestrial Sulfate rock. A whole-rock specimen from Moenkopi formation (USA) is monomineralic, containing primarily gypsum ($CaSO_4 \cdot 2H_2O$); Sulfates are well documented on Mars [7]. The XRD results compare well between the laboratory and the testbed instruments, for this relatively fine-grained sample (Fig. 1). The grain size is estimated to be 15-50 µm, from the spotty rings in the 2D image [8] in Fig. 1. This example illustrates how XRD can discriminate between hydration states using crystal structure, as gypsum has a monoclinic crystal structure which is distinct from orthorhombic anhydrite ($CaSO_4$).

Martian Shergottite. Diffraction data compare well for the basaltic shergottite Zagami (Fig. 2), which contains predominantly the clinopyroxene augite [9].

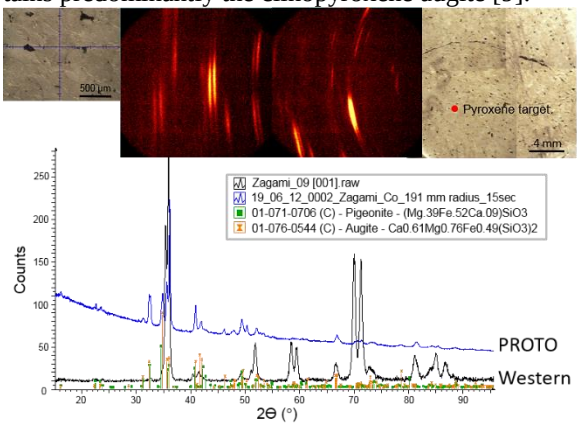

Figure 2. Comparison of lab (Western) and testbed (PROTO) XRD patterns for Zagami martian shergottite - good. Both exhibit augite. Large grain size (~500 µm) results in fewer diffraction lines in lab XRD data due to smaller beam size. Shock-related crystal plastic deformation can be seen as streaking in 2D image from Western (top middle image) [see 10]. Non-representative intensities (preferred orientation) is seen in lab XRD data (e.g. doublets near 59° and 71° 2θ) but the peaks can be recognized as augite by texture in the 2D image. (Inset images are as described in Fig. 1.)

Mars Global Simulant-1 (MGS-1). This martian simulant was designed [11] to replicate Rocknest soil on Mars. Diffraction data are compared in Fig. 3. This simulant was the most challenging sample because it has a variety of grain sizes (representing expected mineral grain sizes in martian soil [11]). The majority of the phases present in the sample were identified by XRD after analyzing multiple targets. Preferred orientation had a major impact on lab-based µXRD identification.

Discussion: X-ray diffraction patterns compare excellently when the material is naturally fine grained. This is because polycrystalline samples contain all lattice planes in diffraction condition simultaneously, and all lattice planes in the ICDD reference pattern are present in the observed XRD pattern. Coarse-grained samples contain fewer lattice planes in diffraction condition

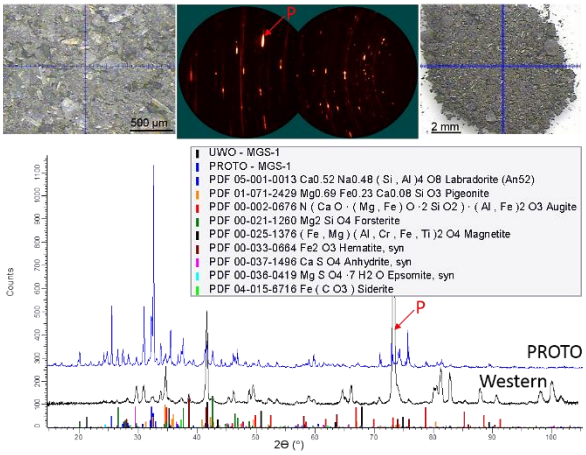

Figure 3. Comparison of lab (Western) and testbed (PROTO) XRD patterns for MGS-1 - poor. Mixture of fine-grained phases (complete Debye rings), coarse-grained material (spotty rings) and very coarse-gained minerals (spots). A large augite crystal oriented in diffraction condition in the small beam of the lab XRD produced non-representative intensities, the most extreme of which is labelled P. (Inset images are as described in Fig. 1.) Note: Data are not background subtracted.

producing fewer diffraction lines and non-representative intensities (preferred orientation), making phase identification less definitive. The situation was more pronounced for the smaller beam diameter used by the lab-based instrument. PROTO's line beam geometry mitigates this situation making single targets more representative of the mineral composition in the rock.

This work lays the foundation for an *in situ* X-ray diffraction instrument to be used in future Mars exploration – or anywhere a remotely-operated robotic rover might be deployed, including remote regions of Earth for environmental science or resource prospecting.

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References: [1] Gellert R. et al. (2006) *JGR*, 111, E02S05. [2] Gellert R. and Clark III B. C. (2015) *Elements*, 11, 39–44. [3] Schmidt M.E. et al. (2018) *JGR Planets*, 123, 1649-1673. [4] Morrison, S. M. et al. (2018) *Am. Mineral.* 103, 848-856 and refs therein. [5] Flemming, R L. (2007) *CJES*, 44: 1333-1346. [6] Rietveld H. M. (1969) *J. Appl. Cryst*., 2: 65–71. [7] Vaniman D. T. et al. (2018) *Am. Mineral.*, 103: 1011–1020. [8] Bramble, M. S., et al. (2015) *Am. Mineral.*, 100: 1899-1911. [9] McCoy, T. J. et al. (1992) GCA, 56: 3571-3582. [10] Jenkins, L.E., et al. (2019) *Meteoritics & Planet. Sci.* 54: 902-918; [11] Cannon K. M. et al. (2019) *Icarus*, 317: 470-478.