HYBRID X-RAY DIFFRACTION FOR PLANETARY MINERALOGICAL ANALYSIS OF UNPREPARED SAMPLES.

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Introduction: A new type of X-ray diffraction (XRD) planetary instrument is being developed based on an innovative hybrid concept that allows performing both powder and single-crystal XRD measurements, making it possible to analyze minerals with limited or no sample preparation. Powder XRD (pXRD), the technique used by the CheMin instrument of MSL [1], will be used when fine-grained samples are presented to the instrument, either in their native state or after preparation with a grinding tool. Single-crystal XRD (sXRD) using polychromatic radiation (Laue diffraction) will be applied when samples are too coarse for pXRD. Laue analysis will allow identification of minerals in unprepared samples and enable ab-initio determination of crystalline phases unknown to current crystallographic databases. In parallel to either diffraction analysis, the instrument will provide X-ray fluorescence (XRF) data for chemical analysis of the sample. A possible implementation of the instrument concept is presented in Figure 1 in the form of a contact instrument fitted to the robotic arm of a rover. Alternatively, the instrument could be installed inside a rover/lander for analysis of delivered unprepared samples.

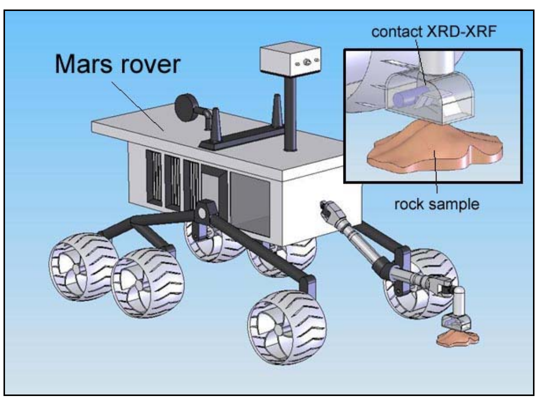

Figure 1. Implementation of a hybrid-XRD / XRF instrument on a rover arm. Other possible implementation is onboard the rover for analysis of "as-delivered" samples (soils, rock fragments, etc)

Powder XRD: Powder XRD, the most common XRD method, requires samples composed of many small crystallites that randomly assume all possible orientations with respect to the incident beam. Generally, good particle statistics requires in excess of 10^6 grains in the analytical volume. With conventional laboratory pXRD instruments, this is achieved with particle sizes of 10 µm or less [2]. With miniature instruments used for planetary deployment, the particle size requirement is even more stringent due to the limited analytical volume imposed by a compact geometry with an acceptable resolution. With the CheMin instrument in MSL, or its commercial spin-off Terra (Figure 2), a particle enhancement method is used that places crushed samples in motion in a vibrated cell, allowing analysis of material up to 150 µm in size [3]. Despite the resulting relaxation on sample preparation requirements, samples must still be collected, crushed and delivered inside a sample cell.

Figure 2. inXitu's Terra portable powder XRD instrument deployed in Spitsbergen during the AMASE 2007 expedition.

Powder diffraction is not strictly limited to prepared powders. Indeed, materials offering very fine crystallite size can analyzed directly without grinding using a reflection instrument geometry. Such instrument was developed jointly by inXitu and the Getty Conservation Institute for the analysis of pigments in art objects, using technologies similar to those used in the Terra transmission instrument (Figure 3)[4]. This instrument is however strictly limited to very fine-grained materials and cannot be applied to an unprepared rock or soil.

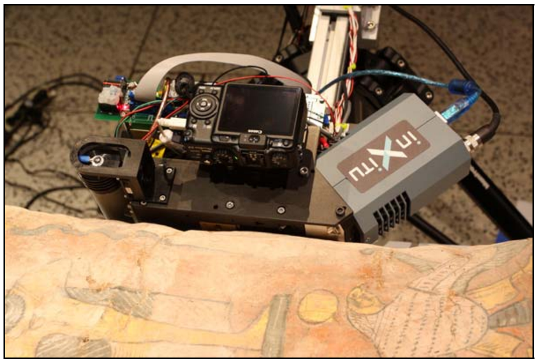

Figure 3. Prototype of miniature powder XRD instrument analyzing surface materials of a Romano-Egyptian Mummy at the Getty Museum (7kg).

Hybrid- XRD instrument concept: The concept will complement a reflection pXRD similar to that shown in Figure 3 with single-crystal diffraction (sXRD) capabilities, using the Laue method. This polychromatic sXRD method does not require complex sample rotations like the more common monochromatic sXRD method. In the Laue instrument, a broad energy spectrum is used in combination with a 2D detector. The main drawback of the Laue method is that data analysis is challenging because non-energy-dispersive detectors cannot discriminate the energy of each diffraction spot observed. The challenges of peak indexing in a Laue diffraction experiment can be overcome easily with application of an energy-dispersive direct-detection CCD, which provides the missing information about the lengths of reciprocal lattice vectors.

A preliminary design was investigated under a NASA SBIR Phase 1 contract to demonstrate the potential of the Laue method for mineral identification. A breadboard instrument was built to test the Laue diffraction capabilities with energy-dispersive CCDs, and software was developed for crystallographic interpretation of these data. An example of a result is presented in Figure 4 that shows the Laue data recorded from an olivine crystal using an energy-dispersive CCD. The image contains 14 diffraction peaks that could be indexed by the software. Major Laue spots could be identified in 30s exposures. With a fully developed and optimized instrument, the method should provide mineral identification capabilities in minutes.

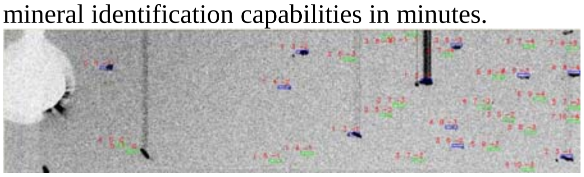

Figure 4. Laue image of olivine marked with Miller indices found by the analytical software. Vertical lines result from the spreading of X-ray signal during CCD readout at positions of intense diffraction

This preliminary study confirmed that the Laue method is useful for mineral identification. A planetary instrument breadboard is under development to fully develop the concept. It will use a collimated beam produced by a 25kV X-ray tube. The characteristic radiation of the tube will be used for powder XRD analysis, and the bremsstrahlung radiation will enable the Laue method. A cluster of 2D detectors collects the diffracted signal over a large solid angle, as illustrated in Figure 5. The same detectors are used to collect either diffraction rings of powder data or Laue diffraction spots. The cluster combines direct detection CCDs for energy discrimination and large CMOS sensors without energy resolution that will provide the coverage to capture a large number of Laue spots over a broad spectral range. Laue spots recorded on the CCDs are sufficient to establish the unit-cell parameters of a crystal.

In parallel to the hardware development, software for data processing and crystallographic analysis will be developed and interfaced to the American Mineralogist Crystal Structure Database (AMCSD).

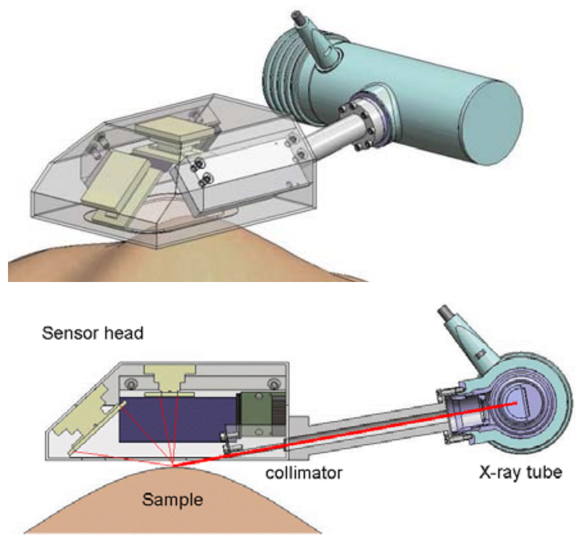

Figure 5 Layout of the critical components of the system; from right to left: X-ray tube, collimator, and sensor head.

References: [1] Blake, D. et al, (2007) *LPS XXXVIII,abstract #1257*. ref chemin [2] Bish D. and J. E. Post, eds. (1989), MSA. Rev. in Min., Vol. 20, 369 pp.; [3] Sarrazin, P. et al, (2004) *LPS XXXV,abstract #1794.* [4] Chiari G. (2008) “Saving Art in-situ”, Nature, Vol. 453, p159