DEVELOPMENT OF SYNCHROTRON 2D AND 3D MICRO-XRD TECHNIQUES APPLICABLE TO THE ANALYSIS OF PICOGRAM MATERIALS RETURNED BY SAMPLE-RETURN MISSIONS.

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Introduction: Synchrotron X-ray techniques have played important roles in previous research of returned, extraterrestrial samples. Notable examples include studies of materials returned by the Stardust and Hayabusa1 probes [1,2]. Primitive Solar System materials, such as those from comets and asteroids and the primary targets of sample return missions, are largely-unequilibrated fine-grained objects and well suited to the high-flux, microfocused analyses these instruments provide. Synchrotron X-ray microdiffraction methods provide the potential to identify rare mineral phases in such samples, with a major advantage being the capability for phase identification within capture media without particle extraction and mineralogic characterization within whole, unsectioned samples. Most of the studies conducted to date, however, were based on single micro-XRD analysis of specific points of interest in the sample, generally defined by other imaging modalities, for example by micro-XRF compositional mapping [e.g., 3, 4]. The goal of this project is to extend micro-XRD analytical capabilities for minute returned materials to an imaging modality including 3D tomography. 3D tomography will provide information regarding the texture of these materials and the crystal structures of the mineral components. In this way, primary minerals, mineralogic zoning within crystallites, orientation relationships, as well as alteration products will be easier to identify.

Methods: Micro-XRD studies to date have focused on developing methodologies for samples that are mineralogically heterogeneous at the micrometer scale. Project goals are to (1) collect interpretable diffraction patterns from picogram samples/voxel, (2) develop reconstruction algorithms to visualize the diffraction features within reconstructed slices of the analyzed materials and (3) convert these into images of mineralogy. It is also desirable to simultaneously collect XRF and XRD data at these high speeds to be able to link observed mineralogies to observed chemical differences.

A new generation of high speed area detectors allow us to collect the diffraction data in mapping mode (including tomography) with accumulation times <100 msec per pixel. For this study, we are utilizing an Eiger X 500K area detector (Dectris), which can collect XRD patterns at frame rates of ~ 1 kHz with pixel sizes of 75 µm. In our experiments, this detector maintains high sensitivity and low backgrounds in the tested configuration. High frame rates are required for minimizing data collection times and small detector pixel size is required to maximize diffraction angle resolution.

Our development work has focused on collecting 3D tomograms from ~500 µm fragments of Murchison (CM) matrix and a CR chondrite (LAP02342). XRD

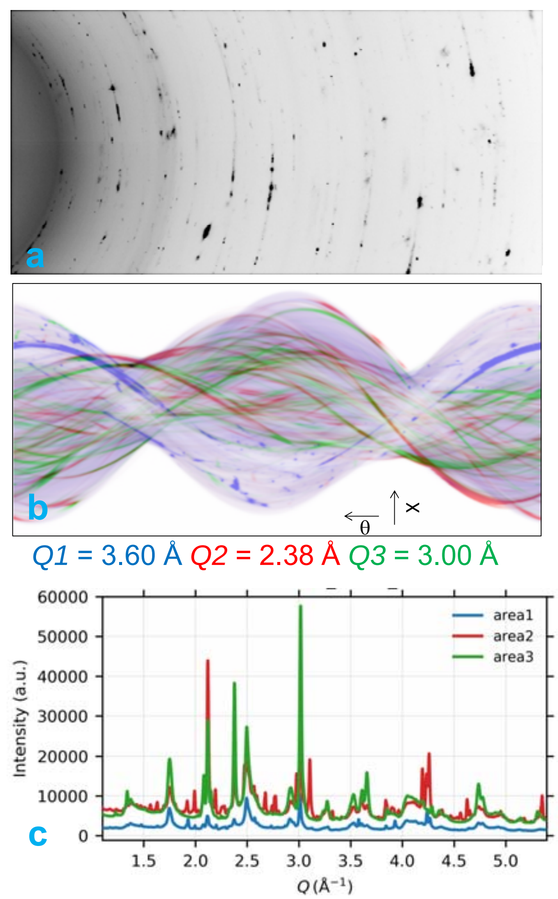

Figure 1: XRD tomographic data for a CR meteorite matrix fragment (LAP 02342). **(a)** Single frame area diffraction pattern from the Eiger detector showing a multitude of diffraction spots from phases in the CR matrix. **(b)**: diffraction sinograms for three Q values. **(c)**: 1D diffraction pattern for areas on the sinogram selected as having individual phase dominance.

and XRF data were collected using a focused 2 μm beam through the sample. XRD data (Fig. 1a) were then collected by scanning the sample through the focused beam horizontally at 2 μm increment size (X) and rotating the sample (θ) at 1 degree increments through 360 degrees of rotation. For these tests, frame rates of 50 msec per pixel were used. Acquisition time for a single tomographic slice using these parameters is ~50 minutes. The sinograms were reconstructed using TomoPy, a python-based open-source framework for tomographic reconstructions [5].

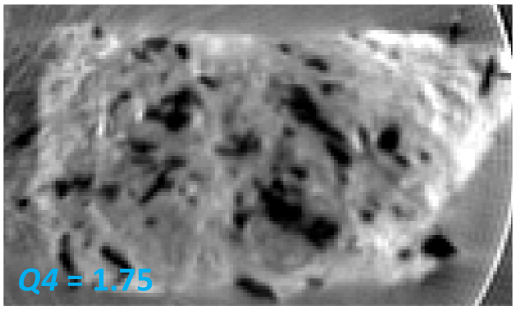

Figure 2: Preliminary reconstructed slice (400 μm wide) for the Q4 (1.75 $Å^{-1}$) diffraction peak derived from serpentine-like minerals.

Results: Figure 1 shows an example of the tomographic data from the CR chondrite sample. The image to the upper left shows an area detector frame collected using a focused 2 μm beam through the sample. Sinograms were generated from the full area detector images for given observed crystallographic reflections (shown in Fig. 1b for reflections at Q = 2.38, 3.00 and 3.60 Å) and then 1D integrated XRD patterns (Fig. 1c) were extracted from the tomograms for localized areas within the CR matrix where each reflection appears to dominate. The image in Fig. 2 shows a preliminary reconstructed slice for Q=1.75 $Å^{-1}$, associated with serpentine-like minerals within the sample. The smallest object in the reconstructed image is near a single pixel, which represents a voxel of dimensions 2 x 2 x 2 μm = 8 $μm^3$ (~20 pg).

Conclusions: Initial testing demonstrates that either two dimensional maps or tomographic slices (scanning horizontal sample position X and angular rotation θ) of XRD data can be collected at frame rates faster than 50 msec per pixel while maintaining excellent signal to noise. We anticipate being able to push this system to even higher scan rates, which should allow us to interrogate both sample chemistry and mineralogy with sufficient sensitivity. Good reconstructions of sample mineralogy can be obtained using conventional tomographic algorithms, but we are in the process of developing new customized computational solutions for reconstructing optimized virtual slices of the mineralogy using these XRD tomograms. These preliminary results are encouraging for producing mineralogical tomograms, a valuable non-destructive approach for characterizing precious returned samples. An important advantage of this approach is that spatially constrained mineralogical data can be obtained, which can then be compared with conventional bulk XRD results, allowing unusual or distinct regions of the sample to be identified for study using other techniques.

References: [1] Flynn G. et al. (2006) *Science, 314*, 1731-1735. [2] Tanaka M. et al. (2013) *Meteoritics & Planet. Sci., 49,* 237-244. [3] Flynn G. et al. (2009) *Adv. in Space Res., 43*, 328-334. [4] Xirouchakis D. et al. (2002) *GCA, 66*, 1861-1874. [5] Gürsoy D. et al. (2014) *Jour. Synch. Rad. 21*, 1188-1193.