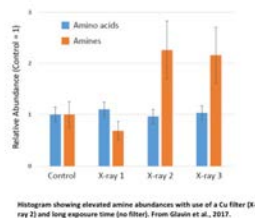


POTENTIAL ALTERATION OF ANALOGUE REGOLITH BY X-RAY COMPUTED TOMOGRAPHY.

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Introduction: The Mars 2020 rover mission will collect and cache samples from the martian surface for possible retrieval and subsequent return to Earth. Mars Returned Samples may provide definitive information about the presence of organic compounds that could shed light on the existence of past or present life on Mars. Post-mission analyses will depend on the development of a set of reliable sample handling and analysis procedures that cover the full range of materials which may or may not contain evidence of past or present martian life [1].

MSR Curation Protocol - Preliminary Examination by X-Ray Computed Tomography: As part of planning for the initial characterization and subsequent distribution to the scientific community, samples would be analyzed while still sealed in their containers using non-destructive, non-invasive techniques. Previous studies [e.g. 1,2] suggest that X-ray Computed Tomography (XCT) may minimally alter samples for most subsequent techniques including organic analyses (Fig. 1). Both [1,2] also point out that the effects of increased radiation on the organics in samples would need to be evaluated, especially for what is expected to be a small native organic signal [3] that would be difficult to detect.



Histogram showing elevated amine abundances with use of a Cu filter (0.2 μm) and long exposure time (no filter). From Glavin et al., 2017.

Organics may be particularly sensitive to lower X-ray energies, a focused X-ray beam, or for longer irradiation times.

Figure 1: As a follow up to their previous work using synchrotron CT, Glavin et al., 2017, and Friedrich et al., 2019, scanned Murchison using the AMNH laboratory uCT instrument to see if polychromatic X-rays would affect the amino acids in Murchison. Three measurements were made at X-ray energies and fluences typical for imaging planetary materials. The results showed little if any effect on the individual in situ amino acids measured from the control, but there were elevated amine abundances, the source of which is unknown.

	Control	X-ray 1	X-ray 2	X-ray 3
Murchison mass (g)	0.5113	0.5048	0.5181	0.5152
X-ray tube potential (keV)	n/a	180	180	180
X-ray tube current (μA)	n/a	120	120	120
Copper filter (0.3 mm)	n/a	no	yes	no
Exposure duration (min)	0	42.2	42.7	459
Total Dose (Gy)	0	~270	~10	~2950

Glavin et al. (2017) reported elevated amines following exposure of Murchison samples with the GE Phoenix v|tome|x s 240 laboratory XCT at the American Museum of Natural History (AMNH).

Evidence for alteration of organics from XCT. Several studies show no alteration of organics (in meteorites) following exposure to monochromatic synchrotron radiation [4,5]. Others [5,6] show that work is needed to quantify the effects of polychromatic laboratory XCT radiation, especially at fluences and energies that will allow in situ examination through the Mars 2020 cache tube. X-rays, transmitted to samples through X-ray tomography, X-ray diffraction, and/or X-ray fluorescence interact with sample materials, potentially producing ionizing radiation. Bertrand et al. [6] suggest that organic rich materials experience a wide range of alteration by both primary and secondary radiation effects from photon energies that approach the carbon absorption edge (Fig. 2).

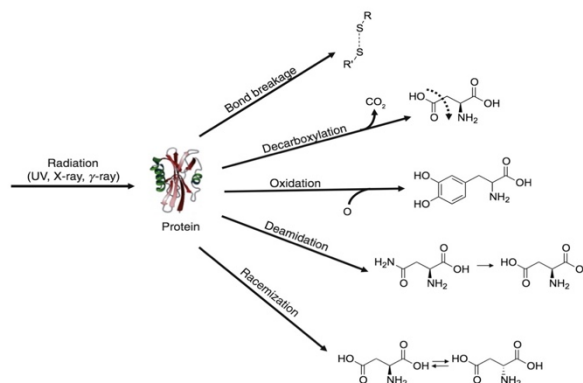


Figure 2: Examples of the types of alteration that organic compounds may experience as a result of primary and secondary effects following X-ray exposure. Image from [6].

Other additional indirect effects may include the creation of chemically reactive by-products, which can react with the original atoms or molecules to form OH radicals or the production of free radicals from macromolecular carbon (MMC) [5]. X-ray radiolysis of functional groups such as amines from an MMC progenitor may mislead conclusions about the origins and composition of the parent material. This combination of effects is the principal mechanism of concern for X-ray alteration of organic-bearing returned samples.

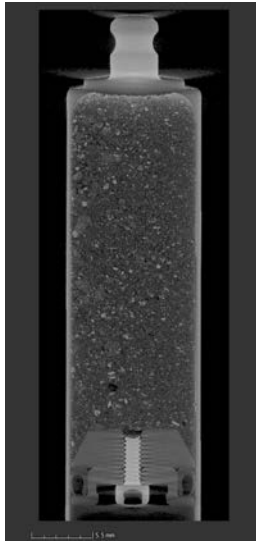


Figure 3: XCT image of a Mars 2020 analogue cache tube, with Mars simulant (<1mm-4mm fragments) and organic compounds inside.

Evidence of sample alteration following XCT scanning. An example set of the Tier I analytes selected for this work [7] were mixed with simulant and loaded into two stainless steel analogue Mars 2020 cache tubes. One tube served as a control and was not exposed while the other was imaged for 545 minutes at 180 kV and 150 μ A using a 1 mm Cu filter.

This initial scan confirmed that a laboratory instrument can penetrate the cache analogue tube based on the calculated linear attenuation coefficient [7] (Fig. 3). A second set of tests were conducted on 4 additional samples, three in similar stainless steel analogue cache tubes and one in a plain glass test tube of the same diameter, using the parameters of Glavin and Friedrich [5,8]. The goal in this experiment was to determine if we could still resolve the analogue regolith materials at lower exposure times as well as identify potential imaging artifacts at parameters currently suggested for the preliminary examination of returned samples from a carbonaceous asteroid [4,5,8].

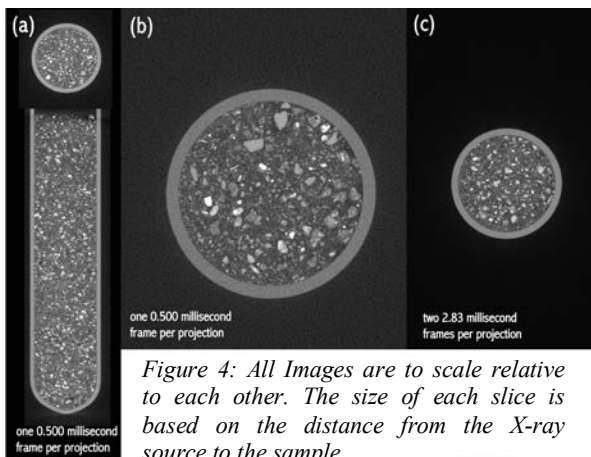


Figure 4: All Images are to scale relative to each other. The size of each slice is based on the distance from the X-ray source to the sample.

Discussion: The 2D reconstructed slices of CT gray values resolve a variety of sub-mm scale materials. However, the higher energy, filtered scans needed to penetrate the highly attenuating tube may remove many of the lower energy photons needed to

resolve lower attenuating phases within grains or for finer grained matrix materials.

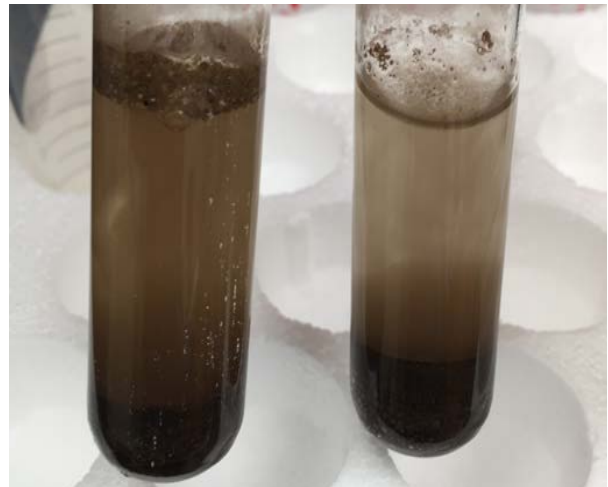


Figure 5: Left tube was exposed to X-rays, the right was the control.

The initial exposed sample (at 545 minutes) was sonicated in ultrapure water as part of developing the organic analysis protocol for LC-MS. There was a clear visual difference between the XCT exposed sample and the control. The exposed sample (on the left in figure 5) had more material in suspension and some stuck along the tube above the fluid meniscus. We postulate that grain size could have been a factor in these visual differences (e.g. finer grains retain a charge following X-ray ionization) but additional work is needed.

References: [1] Kminek, G. et al. (2014) Report of the workshop for life detection in samples from Mars Life Sciences in Space Research 2: p. 1-5. [2] Hanna, R. et al. (2017) Chemie de Erde 77, #4, p. 547-572 [3] Summons R. E., et al. (2014) Astrobiology 14.12 : p. 969-1027. [4] Glavin, D.P. et al. (2017) LPSC XLVIII abstract #1070 [5] Friedrich, J. M. et al. (2016) Meteoritics & Planetary Science 51: p. 429-437 [6] Bertrand, L. et al., (2015) Trends in Analytical Chemistry 66: p. 128-145. [7] Welzenbach, L. C. et al., (2017). 80th METSOC, Abstract #6253. [8] Friedrich, J.M. et al., (2019) MAPS 54, 220-228.