X-RAY COMPUTED TOMOGRAPHY: THE FIRST STEP IN MARS SAMPLE RETURN PROCESSING.

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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. If the samples are returned, that mission would likely present an opportunity to analyze returned Mars samples within a geologic context on Mars. In addition, it may provide definitive information about the existence of past or present life on Mars.

Mars sample return presents unique challenges for the collection, containment, transport, curation and processing of samples [1] Foremost in the processing of returned samples are the closely paired considerations of life detection and Planetary Protection. In order to achieve Mars Sample Return (MSR) science goals, reliable analyses will depend on overcoming some challenging signal/noise-related issues where sparse martian organic compounds must be reliably analyzed against the contamination background. While reliable analyses will depend on initial clean acquisition and robust documentation of all aspects of developing and managing the cache [2], there needs to be a reliable sample handling and analysis procedure that accounts for a variety of materials which may or may not contain evidence of past or present martian life.

A recent report [3] suggests that a defined set of measurements should be made to effectively inform both science and Planetary Protection, when applied in the context of the two competing null hypotheses: 1) that there is no detectable life in the samples; or 2) that there is martian life in the samples. The defined measurements would include a phased approach that would be accepted by the community to preserve the bulk of the material, but provide unambiguous science data that can be used and interpreted by various disciplines. Foremost is the concern that the initial steps would ensure the pristine nature of the samples. Preliminary, non-invasive techniques such as computed X-ray tomography (XCT) have been suggested as the first method to interrogate and characterize the cached samples without altering the materials [1,2]. A recent report [4] indicates that XCT may minimally alter samples for some techniques, and work is needed to quantify these effects, maximizing science return from XCT initial analysis while minimizing effects.

Computed X-Ray Tomography of Planetary Materials: XCT has seen a significant increase in its application to planetary science research in the last decade, with more dedicated facilities to support increasing demand, and the development of sophisticated instruments to meet the requiremets posed by unique materials[5,6]. Using X-ray photons, XCT generates three-dimensional (3D) images of geologic materials, allowing for rapid, non-invasive, non-destructive visualization analyses of the interior of opaque materials. For planetary science, this is especially useful for interrogating small, rare, or valuable materials for specific features or structures, which helps to inform decision making about sub-sampling and curation [7]. Visualization by contrast of in situ components such as metal grains, vesicles, breccia clasts, the structures and shapes of chondrules, or low-Z materials such as halite have allowed more complete interpretations of parent body formation and evolution, by revealing many details in a context that would otherwise be lost or damaged in processing.

PAT 91501-In Situ Whole Rock Study: The XCT study of the Antarctic meteorite PAT 91501 provided one of the earliest studies of a rare assemblage of metal/sulfide grains and associated voids (vesicles) to determine the formation conditions without disassembling the main mass. [8]

Kobe meteorite for characterization and curation: The Kobe (CK4 chondrite) meteorite was used by JAXA as a test case for quanitifying compositional examination and curation by micro-XCT. Results were then used to develop methodologies for processing returned samples from the HAYABUSA mission [9,10]

XCT for Sample Return Processing: In 2014, *The Report of the Workshop for Life Detection in Samples from Mars* [3] was published as an update to the 2001 Planetary Protection Draft Test Protocol. The update incorporates new findings and technological advances through community input, a comprehensive list of sample handling procedures, and analytical measurements for returned Mars samples in the context of life detection and Planetary Protection. Assuming initial established protocols and procedures for controlled processing have been followed (Figure 1), the next step would be to address the method for characterizing sam-

Table 1
Proposed sequence for sample analysis. For the specific types of analysis see Table 2.

Sequence for sample analysis	Sample condition	General type of analysis
I	Sample acquisition on Mars	Remote and *in-situ* analysis on Mars to characterise the sample type and the geological context
II	Any solid sample material on the outside of the sample containers	Solid sample analysis; full sequence (non-destructive & non-invasive, non-destructive & minimal invasive, and destructive)
III	Head space gas	Gas sample analysis; full sequence
IV	Solid samples in containers	Solid sample analysis; non-destructive & non-invasive
V	Solid samples removed from containers	Solid sample analysis; non-destructive & minimal invasive
VI	Fluid inclusions from solid samples removed from containers	Liquid sample analysis; full sequence
VII	Solid sample removed from containers	Solid sample analysis; non-destructive & minimal invasive, destructive

Table 2
Examples for types of sample analysis with a focus on life-detection. The detailed processing of the solid samples would depend on their nature, e.g., rocks, regolith, sand, and requires proper contamination control. FTICR-MS: Fourier Transform Ion Cyclotron Resonance Mass Spectrometry; GC-IRMS: Gas Chromatography Isotope Ratio Mass Spectrometry; GC-MS: Gas Chromatography Mass Spectrometry; IR: Infrared; LC-MS: Liquid Chromatography Mass Spectrometry; SEM: Scanning Electron Microscopy; TEM: Transmission Electron Microscopy; TOF-SIMS: Time of Flight Secondary Ion Mass Spectrometry; UV: Ultraviolet; XANES: X-Ray Absorption Near Edge Spectroscopy; XRD: X-Ray Diffraction.

Invasiveness	Solid sample analysis	Gas sample analysis	Liquid sample analysis
Non-destructive & non-invasive	• 3D X-ray micro-tomography • Surface imaging and spectroscopy	Not applicable	Not applicable
Non-destructive & minimal invasive (no specific sample preparation)	• Microscopy • Fluorescence • IR, visible, UV, deep UV spectroscopy • SEM	• IR, visible, UV, deep UV spectroscopy	• Microscopy • Fluorescence • IR, visible, UV, deep UV spectroscopy
Destructive (specific sample preparation)	• SEM, TEM, nano-X-ray-tomography • XRD, XANES • GC-MS, GC-IRMS, FTICR-MS, LC-MS, TOF-SIMS, Nano-SIMS • Target independent biopolymer sequencing	• GC-MS, GC-IRMS, FTICR-MS, LC-MS	• GC-MS, GC-IRMS, FTICR-MS, LC-MS, TOF-SIMS, Nano-SIMS, • Target independent biopolymer sequencing, flow cytometry

Figure 1-Tables 1&2 from Kminek et al. (2014) [3] showing the proposed squence and types of sample analysis for MSR. XCT analysis of MSR samples would occur while still encapsulated; step IV of Table 1.

ples and planning for their distribution to the scientific community. Samples would be analyzed while still sealed in their containers with non-destructive, non-invasive techniques. XCT analysis would provide a three-dimensional whole sample reference, reveal physical heteorogeneities at micron-level resolution including fractures, veins, porosity, lithologic and possibly mineralogical based structures. Higher dose X-rays (e.g. synchrotron radiation) would allow compositional details such as elemental distribution and mineralogy. The report points out that the effects of increased radiation on the samples would need to be evaluated. In particular, the effects of XCT radiation on organics in returned martian samples are considered to be of critical importance.

Problems with XCT?: A recent study provides a contrasting perspective that suggests that XCT [at doses that are considered non-destructive] does alter planetary materials. Sears et al. (2016) [4], have shown that XCT deposits sufficient radiation to alter the natural radiation record of a meteorite. While characteristics such as thermoluminescence may be limited to certain types of studies, it brings to the fore the need to properly document and quantify the effects of XCT radiation on a variety of materials, especially when moving to higher excitation energies to determine composition.

Next Steps: In order to properly evaluate the potential impact XCT may have on returned samples, a detailed study to quantify the radiation dosage is required. Because XCT systems can be configured for a variety of sources, detectors and geometric configurations[5,6,7], a long term study of a variety of materials using multiple instruments is required. We will dope martian regolith simulants and basalt analog samples with a variety of organic compounds to document changes that may occur from XCT radiation. Results will be quantified with techniques appropriate (e.g. Raman spectroscopy or mass spectrometry) to better understand which classes of compounds are most susceptible and the subsequent products that may be produced. The materials will be tested using instruments at NASA Johnson Space Center, the National synchrotron Light source II at Brookhaven National Lab, and the Natural History Museum in London.

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