PREPARING FOR MARS SAMPLE RETURN: *IN-SITU* X-RAY DIFFRACTION MEASUREMENTS USING THE NATIONAL SYNCHOTRON LIGHT SOURCE-II AT BROOKHAVEN NATIONAL LABORATORY. J. A. Hurowitz[1], J. Thieme[2], J. Bai[2], E. Dooryhee[2], E. Fogelqvist[3], J. Gregerson[1], M. A. Schoonen[1,2], K. A. Farley[4], and S. Sherman[4], [1]Department of Geosciences, Stony Brook University, Stony Brook, NY 11794, joel.hurowitz@stonybrook.edu, [2]Brookhaven National Laboratory, Upton, NY, [3]Royal Institute of Technology/Albanova, Stockholm, SWE, [4]California Institute of Technology-Jet Propulsion Laboratory, Pasadena, CA.

Introduction: Beginning in the year 2020, NASA will embark on the first step of what may be an ambitious, multi-mission campaign with the objective of returning a scientifically selected cache of rock, regolith, and atmosphere samples from Mars for analysis in laboratories on Earth. The primary goal of these analyses will be to determine whether or not Mars was ever host to ancient microbial life [1]. A positive result for extinct (or extant) life on Mars has the potential to fundamentally alter our view of the origin and evolution of life, by providing proof that the Earth is not unique when it comes to the question of biological activity in the Solar System. These returned Martian samples will have tremendous additional value beyond questions of extraterrestrial life; providing a rich repository of information on the history of planetary accretion and differentiation, geochronology, atmospheric evolution, and the paleo-environmental history of Mars [1]. Indeed, the potential scientific understanding to be achieved with this cache of samples will equal or exceed that of the Apollo lunar sample archive, which continues to yield new insights on the history of the Solar System, over 40 years after they were returned to Earth (e.g., [2]).

Any laboratory that proposes to fill the role of Sample Receiving Facility (SRF) for Martian samples will be subject to the strictest Planetary Protection requirements, established to protect the Earth from potentially dangerous extant life associated with the returned Martian sample cache, and to prevent “false positives” for Martian life arising from terrestrial biological contamination [3]. Accordingly, the development timeline required to design, build, and test an SRF suitable to house Martian samples is likely to be on the order of a decade [4]. Given that samples are likely to be returned from Mars in the early 2030’s, the time to provide proof-of-concept measurement data to establish the feasibility of sample handling and safe sample triage in an SRF facility is now. The high X-ray brightness of the National Synchrotron Light Source-II (NSLS-II) at the Brookhaven National Laboratory provides a unique and critical capability to perform *in-situ* assessments of mineralogy (using X-ray diffraction, XRD), sample integrity (using X-ray tomography), chemistry and molecular identity (using X-ray fluorescence [5], and X-ray Raman scattering), immediately after samples are returned to Earth, but before they are unsealed from their collection tubes. *In-situ* sample triage measurements like these are viewed by NASA and the Office of Planetary Protection as required steps before samples are allowed to leave containment.

Here, we describe a set of proof-of-concept measurements, conducted at the X-ray Powder Diffraction beamline (XPD-28ID-2) at NSLS-II in late November 2016, which demonstrate the capability to quantitatively assess the mineralogy of rock samples encapsulated in Ti-alloy tubes. These tubes are prototypes of those that will be used during the Mars 2020 Rover mission to encapsulate rock and regolith samples that could be returned to Earth. Accordingly, the measurements described here are a high-fidelity test of our capability to conduct valuable triage measurements on samples returned from Mars.

Materials & Methods: Six samples (each approx. 2 cm long, 1.5 cm diam) were collected using the coring drill prototype for the Mars 2020 Sample Caching System (SCS) at the NASA Jet Propulsion Laboratory (JPL). These samples consist of three igneous rocks: (i) basalt, (ii) tuff, (iii) pumice, and three sedimentary rocks: (i) basaltic sandstone, (ii) lacustrine mudstone, (iii) bedded gypsum. The samples are named VSB, BTI, ODP, NBS, KMM, and CRG, respectively.

The samples were manually loaded into an SCS prototype Ti-6Al-4V alloy tube (**Fig. 1**) at the XPD beamline, with foam packing between each sample. The tube was then attached to a rotary translation stage (**Fig. 2**). This stage allowed the sample tube to be rotated continuously, or in fixed increments, and translated horizontally, thereby allowing X-rays to interrogate the full contents of the loaded sample tube. Each sample could be readily located within the tube by comparing the intensity of the x-ray beam transmitted through the foam separators and the rocks. For most of our measurements, the sample tube was rotated continuously and translated laterally in ~2.5 mm increments while successively exposing each sample to the X-ray beam, yielding volume-averaged X-ray diffraction patterns at five distinct positions in each sample. A ~1mm diameter beam of monchromatic X-rays (E=67.756 KeV, λ=0.1830 Å) was directed at the sample tube and diffracted X-rays were transmitted through the sample tube to a 2D flat-panel detector located approximately 1.5 m from the sample tube. 63% of the x-ray beam is transmitted through, i.e. x-rays are a sufficiently "hard"/penetrating probe for the photo-absorption effects to not corrupt the measured diffracted signal. Each individual diffraction pattern was collected with a 30-60 sec. integration time.

Results: Representative results from our preliminary data analysis are shown on **Fig. 3**, where an X-ray diffraction pattern from a single volume-averaged scan through each sample is plotted as a function of X-ray intensity versus 2-theta (2Θ) angle. Each pattern is of sufficient quality to enable mineral phase ID and estimates of mineral abundance, and each sample is clearly distinguished on the basis of its unique diffraction pattern, despite the fact that all were analyzed in transmission through 1.5 cm of sample thickness, and encapsulated in a Ti-alloy tube with 0.5 mm thick walls. Features that can be readily discerned in the patterns include: (i) amorphous components in the BTI and ODP scans at 2-3^{o} (2Θ), consistent with the presence of volcanic glass, (ii) mineralogical similarity between the VSB basalt and the NBS basaltic sandstone, (iii) a low-angle reflection at ~1^{o} (2Θ) in the KMM sample, consistent with the presence of a phyllosilicate phase, (iv) numerous diffraction doublets, readily observed in all patterns at 10-12^{o} (2Θ), generated by diffraction from both sides of the Ti-alloy tube.

Future Plans: Near-term work will include mineral phase identifications and phase abundance estimates for all samples, including an assessment of differences between scans collected within individual samples at variable translation distances and rotation angles. In addition, we will conduct a new set of *in-situ* Pair Distribution Function analyses on a set of samples that are composed partly or entirely of X-ray amorphous components (including BTI and ODP). These experiments, planned for mid-January at the XPD beamline, may provide a first-step towards discerning the identity and short-range order of amorphous materials in Martian samples while encapsulated in their collection tubes. X-ray amorphous materials of variable composition have proven to be a significant component of all samples analyzed by XRD during the *Curiosity* rover mission to Mars (e.g., [5]). Finally, our long-term goal is to develop the capability for 3D tomograpic-imaging and tomographic-diffraction on encapsulated samples.

References: [1] McLennan, S.M. et al. (2011) Final report of the MSR E2E-iSAG, MEPAG, p. 101. [2] McCubbin, F.M., et al. (2010) *PNAS* 107, 11223-11228. [3] COSPAR (2002) The Quarantine and Certification of Martian Samples, The National Academies Press. [4] Smith, C., et al. (2016) iMARS Phase II: Findings and Recommendations, MEPAG Annual Meeting, Silver Spring, MD. [5] Thieme, J., et al., this

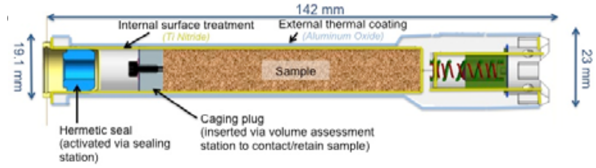

Fig. 1: Schematic illustration of a hermetically-sealed Ti-alloy tube to be used for encapsulating samples on the Martian surface prior to Earth return.

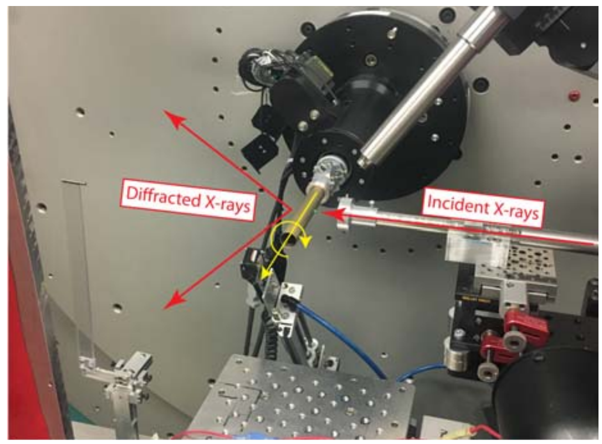

Fig. 2: Image of the Ti-alloy sample tube at the XPD beamline. Red arrows indicate the vectors of incident and diffracted X-rays, while yellow arrows indicate the rotary and horizontal translation directions of the sample stage, which enable analysis of all of the sample material encapsulated within the tube.

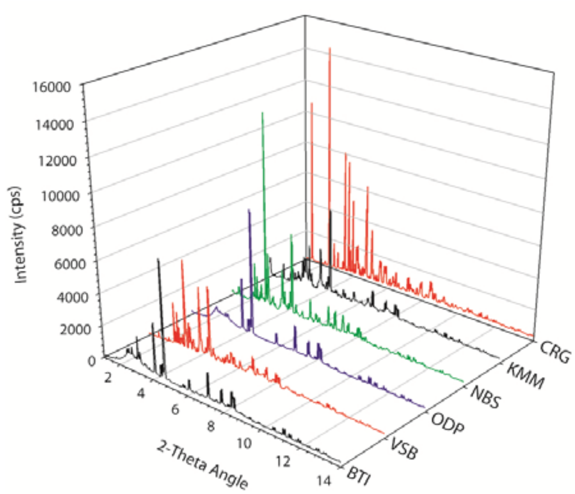

Fig. 3: Representative X-ray diffraction patterns for the 6 samples investigated in this study, plotted in 3D as a function of intensity (cps) versus 2-theta angle.