

**ELEMENTAL COMPOSITION OF ANALOGS TO SAMPLES RETURNED FROM MARS USING X-RAY FLUORESCENCE IMAGING AT THE NATIONAL SYNCHOTRON LIGHT SOURCE-II AT BROOKHAVEN NATIONAL LABORATORY.** J. Thieme<sup>1</sup>, J. A. Hurowitz<sup>2</sup>, E. Dooryhee<sup>1</sup>, E. Fogelqvist<sup>3</sup>, J. Gregerson<sup>2</sup>, M. A. Schoonen<sup>1,2</sup>, K. A. Farley<sup>4</sup>, and S. Sherman<sup>4</sup>, <sup>1</sup>Brookhaven National Laboratory, PO Box 5000, Upton, NY 11973, [jthieme@bnl.gov](mailto:jthieme@bnl.gov), <sup>2</sup>Department of Geosciences, Stony Brook University, Stony Brook, NY 11794, <sup>3</sup>Biomedical & X-ray Physics, Dept. of Appl. Phys., KTH/Albanova, SE-10691 Stockholm, Sweden, <sup>4</sup>California Institute of Technology-Jet Propulsion Laboratory, 4800 Oak Grove Drive, Pasadena, CA 91109.

**Introduction:** In 2020, NASA will launch out into the first step of what may be an ambitious, multi-mission campaign with the goal to bring back for analysis in laboratories here to Earth a collection of rock, regolith, and atmosphere samples from Mars. It is the main objective of this endeavor to determine whether or not Mars was ever host to ancient microbial life [1]. Finding evidence for extinct (or extant) life on Mars has the potential to fundamentally alter our view of the origin and evolution of life. It would provide proof for Earth being just one amongst others regarding the question of biological activity in the Solar System. Furthermore, returned Martian samples would provide a rich repository of information on the history of planetary accretion and differentiation, geochronology, atmospheric evolution, and the paleo-environmental history of Mars, adding tremendous additional value to such a mission beyond the issue of extraterrestrial life [1]. The potential knowledge to be obtained by such a collection of samples will equal or exceed that of the Apollo lunar sample archive, which even today yields new insights on the history of the Solar System, over 40 years after they were returned to Earth (e.g., [2]).

Strictest Planetary Protection requirements will be stipulated to any laboratory proposing to take on the role of a Sample Receiving Facility (SRF) for Martian samples. These have been established to protect the Earth from potentially dangerous extant life associated with the returned Martian sample cache, as well as to prevent “false positives” for Martian life arising from terrestrial biological contamination [3]. Essentially, the timeline for designing, building, and testing an SRF suitable to receive and work with Martian samples is likely to be on the order of a decade [4]. Thus, as samples might be returned from Mars in the early 2030’s, it is now time to provide proof-of-concept measurement data to establish the feasibility of sample handling and safe sample triage in an SRF facility. 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 to perform *in-situ* assessments of mineralogy (using X-ray diffraction [5]), assessments of the elemental composition and the chemical state (using synchrotron radiation X-ray fluorescence (SXRF) imaging and X-ray absorption near-edge structure (XANES)

spectroscopy, both with high spatial resolution) after samples are returned to Earth.

The experimental procedure is to transfer the samples into an X-ray transparent sleeve from the primary Ti-alloy sleeve under controlled conditions to avoid exposure to the terrestrial atmosphere. We envision that the transfer could be done in a controlled area (specialized glove box) that prevents exposure and contamination of the sample. As shown in **Fig. 1**, materials such as BeO ceramic or polycarbonate are X-ray transparent in an X-ray energy range used for XRF experiments. This allows for the samples to be studied by SXRF techniques, well-established at NSLS-II.

XRF mapping and XANES imaging experiments to investigate the elemental composition and the chemical state of a sample with sub- $\mu\text{m}$  and sub-100nm spatial resolution are the core capabilities of the SRX beamline [6]. Elemental maps can be obtained from a sample in 2D and in 3D. The X-ray energy useful for such experiments is situated in the region of about 5-25 keV. Within this energy region, a wide range of elements show X-ray absorption edges, yielding detailed chemical information. To investigate a Martian sample as a whole, the penetration ability of these X-ray energies is not enough. However, a shell or layer of the sample with a thickness of a few mm can be investigated. This will be possible for Martian return samples, when they are transferred into X-ray transparent sample containers, as has been shown in this proof-of-principle experiment (see **Fig. 2** and **Fig. 3**).

These experiments have been performed in late November 2016, demonstrating the capability to obtain elemental composition and chemical speciation information of rock samples when encapsulated in X-ray transparent material. BeO ceramic material has been used to cover the rock sample, testing the encapsulation. The measurements represent a high-fidelity test of our capability to conduct valuable XRF and XANES measurements on samples returned from Mars.

**Materials & Methods:** Six samples (each approx. 2cm long, 1.5cm 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.

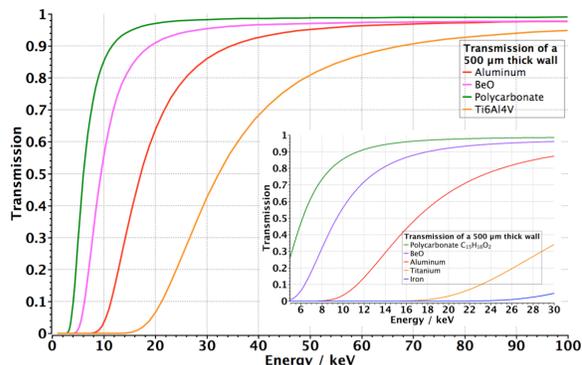
The samples were manually fixed onto a standard sample holder, which subsequently was attached to the scanning stages at the SRX beamline. X-rays, focused by SRX optics, illuminated a sub-micron sized spot on the sample; the created X-ray fluorescence is collected by an energy dispersive detector. The stages moved the sample across the X-ray spot, thus generating a 2D map of the elemental composition of this sample (see Fig. 2). By fine-tuning the X-ray energy across an absorption edge of one chemical element with the monochromator of the SRX beamline, a XANES spectrum can be obtained (see Fig. 2).

**Results:** X-ray fluorescence maps have been taken of all samples described above; Fig. 3 shows the data obtained for the KMM sample. The samples have been illuminated with an X-ray energy of 12 keV. The spectrum shows that even with a 500µm thick BeO ceramic covering the rock, XRF signals down to low-Z elements such as Ca or Ti around 4 keV are clearly identifiable. The XRF images in figure 2 (150x150 µm<sup>2</sup>, step size 1 µm, dwell time 0.3 sec) show the heterogeneity of the elemental distribution in this sample. The scale bar indicates the XRF signal strength, which shows that the distribution can be detected on a wide range of elemental concentrations. In principle, XRF is capable of measuring concentrations down to the ppm-level. Fig. 2 shows XANES spectra of an iron-rich spot of a sample. The spectra have been measured without and with a BeO ceramic plate of 500 µm thickness in the path of both, the incident X-ray beam and the fluorescence X-rays measured by the detector. The spectra are identical, showing that the impact of the BeO plate is negligible.

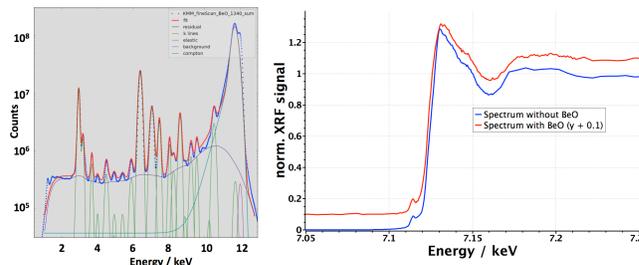
*Future Plans:* Near-term work will include the collection of more chemical information for all samples, e.g. additional XRF maps to improve statistics and additional XANES spectra from elements present in the samples. In addition, we will conduct experiments using the upcoming SRX capability of mapping and spectroscopy at sub-100nm spatial resolution. The chemical coordination of a probed element can be determined using extended X-ray absorption fine structure (EXAFS) spectroscopy, which is another SRX capability to be applied to these 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] Hurowitz, J., et al.,

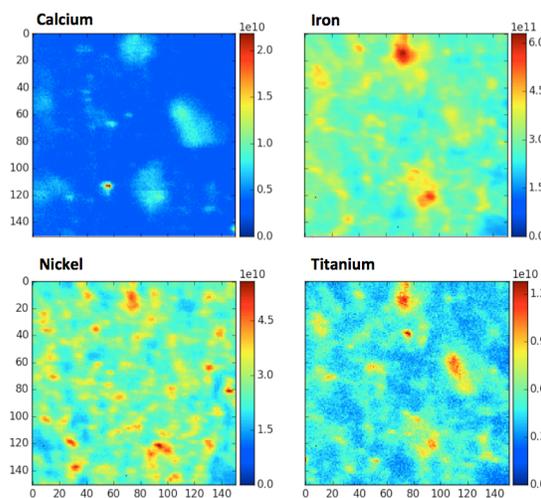
this conference. [6] de Andrade, V. et al. (2010) Nuclear Instruments and Methods in Physics Research A 649, p. 46–48.



**Fig. 1:** Transmission of a 500 µm thick wall of four different materials as a function of X-ray energy up to 100keV. The inset magnifies the energy range to 30 keV.



**Fig. 2:** Left: XRF spectrum from a lacustrine mudstone, KMM, covered by a 500µm thick BeO ceramic plate. Right: XANES spectra of an iron-rich spot of a sample with and without the BeO ceramic cover. The spectrum with BeO has been shifted in y for better comparison.



**Fig. 3:** XRF images of an 150x150 µm<sup>2</sup> are of KMM, showing the spatial distribution of the elements Ca, Ni, Fe, and Ti within the sample.