

IRON NANOPARTICLES AND ILMENITE-LIKE SIGNATURES REVEALED BY SOFT X-RAY SPECTROSCOPY OF APOLLO 17 CORE 73002 SAMPLES. R. A. Colina-Ruiz¹, T. Kroll¹, R. Walroth¹, J. P. Bradley², H. A. Ishii², D. Sokaras¹, J.J. Gillis-Davis³, ¹SLAC National Accelerator Laboratory, Menlo Park, CA 94025, ²Hawai'i Institute of Geophysics and Planetology, Honolulu, HI 96822, ³Department of Physics, Washington University at St. Louis, St. Louis, MO 63130

Introduction: In late 2019, as part of the Apollo Next Generation Sample Analysis (ANGSA) initiative, the double drive tube from Apollo 17, station 3 (73002/73001), was opened. The bottom part of the drive tube (73002) was sealed in a Core Sample Vacuum Container (CSVC) on the Moon by the astronauts. These specially curated samples were kept unopened and pristine for nearly 50 years, so they could be studied using modern instrumentation and methodologies. For our ANGSA investigation we employed synchrotron-based soft X-ray absorption spectroscopy (XAS) and X-ray emission spectroscopy (XES) on samples from specially curated 73002 and previously opened but still pristine drill core samples 70003-70009. These techniques reveal information related to coordination chemistry, and identity and charge state of atomic bounds that could lead to characterization of structural defects.

We use our XAS and XES measurements of ANGSA samples to examine a debate about the oxidation state of lunar regolith components. One hypothesis expects that the lunar regolith becomes more reduced with accumulation of solar wind implantation protons [1]. In contrast, TEM-based electron energy-loss spectroscopy (EELS) data shows a trend of increasing oxidation state with soil maturity for Fe nanoparticles (npFe⁰) [2]. XAS/XES measurements of 40 mg allquots taken from each specially curated core provide overall picture of regolith oxidation state. These data record whether oxidation occurs with accumulated exposure to the space environment or whether it takes place during typical curation with a dry nitrogen.

Samples and Experimental details: A suite of samples from different depths within the 73002 upper drive tube were collected and analyzed for composition [3] and maturity [4] (e.g., 7.6wt.%<FeO<8.5wt.%; 1.2wt.%<TiO₂<1.8wt.%; I_s/FeO 20-70). I_s/FeO values from [4] were compared to the XAS- XES-based redox states of the samples. 73002 core samples were compared with previously opened 70003-70009 cores samples. Ti L_{3,2}-edge, O K-edge, and Fe L_{3,2}-edge XAS spectra were acquired at beamline 10-1 at the Stanford Synchrotron Lightsource (SSRL). Data acquisition mode allows probing samples to a ~2 nm depth, where space weathering effects are dominate. Si K_β XES spectra were collected at SSRL beamline 6-2a.

Results and discussions: Fe L_{3,2}-edge XAS spectra are shown in Figure 1. Signatures of multiple oxidations states (Fe³⁺, Fe²⁺ and Fe⁰) are presented. The presence of

Fe⁰ is similar to previously reported nanoparticles. Data for the previously opened samples point to higher oxidation state in comparison to the specially curated samples from 73002. Terrestrial oxidation effects could be evidenced from Fe L_{3,2}-edge. From Ti L_{3,2}-edge XAS spectra in Figure 2, exhibit four main peaks (A to D) that are ascribed to the 2p⁶3d⁰→2p⁵3d¹ transitions of Ti⁴⁺ ion to the states of t_{2g} (peaks A and C) and e_g (peaks B and D) regardless of the distortion of the octahedral crystal-field symmetry in FeTiO₃ ilmenite. The typical splitting due to the reduced symmetry of O_h in TiO₂ anatase is not observed pointing to ilmenite-like distortions.

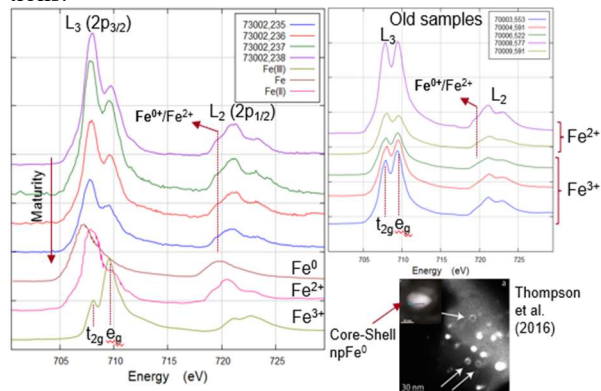


Figure 1. Fe L_{3,2}-edge normalized XAS spectra for (left) 73002 recently opened core samples and references and (right) 70003-70009 typically curated core samples. A TEM micrograph from [3] revealed npFe⁰ that could be observed on the spectra.

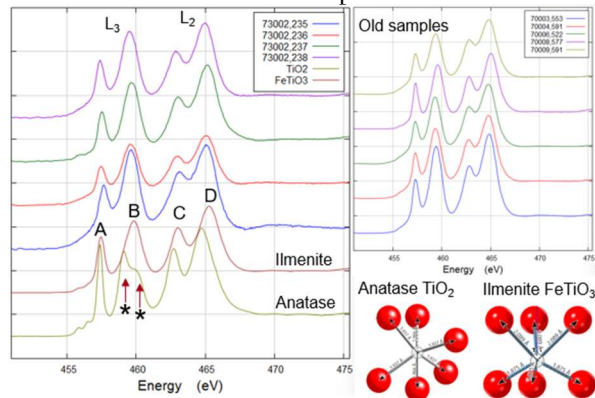


Figure 2. Ti L_{3,2}-edge normalized XAS spectra for (left) 73002 recently opened core samples and (right) 70003-70009 typically curated core samples. TiO₂ and FeTiO₃ first coordination shells are shown.

Electronic structure around O revealed differences between recently opened samples and previously opened samples as is shown in Figure 3. Peak around 532 eV in O K-edge to O $1s$ electron transition to π^* orbital states of O_2 . The previously opened samples show a splitting related to this feature that point to an increase in the hybridization degree and could be related to higher oxidation previously observed from Fe $L_{3,2}$ -edge. Therefore, from O K-edge we could be tracking Fe oxidation due to the diffusion of O atoms to the surface of the $npFe^0$ embedded in oxygen-rich matrix that surrounds them. Feature around 536 eV is associated with $1s$ to $2p$ electronic states hybridized with Si $1s$ and $3p$ states in tetrahedral coordinated SiO_2 . Then, in overall, O K-edge point to a SiO_2 -like spectrum (No t_{2g} - e_g splitting is observed) expected due to the silicate nature of the samples.

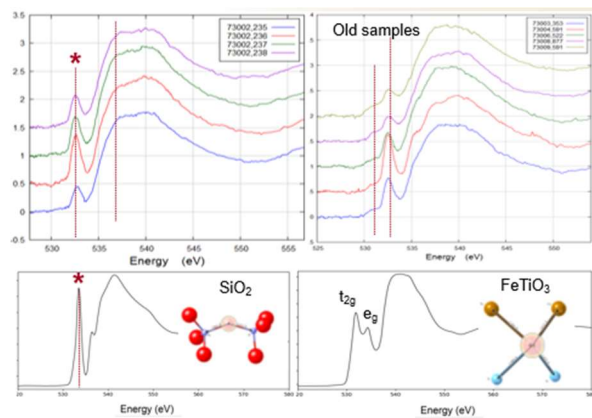


Figure 3. O K-edge normalized XAS spectra for (left) 73002 recently opened core samples and (right) 70003-70009 old core samples. TiO_2 and $FeTiO_3$ reference spectra are also shown.

Conclusions and Outlook: Apollo 17 core 73002 samples with different depth and maturity were studied from a multi-edge approach to reveal the local electronic structure and signatures of oxidations from Fe such as relevant features from Ti. $npFe^0$ have been detected from Fe $L_{3,2}$ -edge XAS overall data such as signatures of Fe^{2+} and Fe^{3+} . Previously opened core samples with long exposure to the dry nitrogen used in curation could be oxidizing Fe species, traces of Fe^{3+} are more evident. First coordination shell symmetry shows high-degree of distortions around Ti and revealed ilmenite-like signatures in core 73002 samples. Expected Ti^{4+} overall oxidation state was corroborated. Lattice dynamics from O K-edge could explain possible Fe oxidation effect in earth. Si K_{β} XES spectra is under analysis and is expected to get information related to hydroxyl- and peroxo-bearing species due to its sensibility to protonation states of bound species and it will be compared to O K-edge XAS. EELS measurements will

be included to get higher resolution information about Fe oxidation. Finally, these results in regolith from Ti $L_{3,2}$ -edge, where low-Ti content samples (<2wt.%) data have been obtained, will work to starting point to future studies in high-Ti basalt samples (where ilmenite have found and addressed as primary potential resource for oxygen and other raw materials to supply future lunar bases, due to the high sensibility. 73001 core samples, that were specially sealed on the Moon will be analyzed using XAS and XES techniques in the near future. These bulk analytical techniques will be compared with higher spatial resolution TEM data acquired by Co-Is Ishii and Bradley.

References: [1] Papike *et al.* (2005) American Mineralogist 90:277-290. [2] Thompson *et al.* (2016) Meteoritics & Planetary Science 51: 1082-1095. [3] Neuman *et al.* (2022) 53rd LPSC, abstract #1567. [4] Morris *et al.* (2022) 53rd LPSC, abstract #1849.

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