Laboratory Analysis of Returned Samples
Abstracts of Selected Proposals
(NNH20ZDA001N-LARS)

Below are the abstracts of proposals selected for funding for the Laboratory Analysis of Returned Samples program. Principal Investigator (PI) name, institution, and proposal title are also included. **30** proposals were received in response to this opportunity. On January 11, 2021 **7** proposals were selected for funding.

Timothy Glotch/State University Of New York, Stony Brook
Coordinated Infrared, X-ray, and TEM Analyses of CI and CM Chondrites in Preparation for Small Body Sample Return

The goals of the proposed work are to (1) conduct a set of coordinated infrared, X-ray, and transmission electron microscopy measurements of primitive chondrites in preparation for analysis of returned samples from Bennu and Ryugu, and (2) develop visible/near-infrared (VNIR) and mid-infrared (MIR) nano-IR hyperspectral imaging techniques for analysis of returned samples.
Based on VNIR and MIR spectroscopy of meteorite analogs and the asteroids Bennu and Ryugu, it is likely that samples returned by the OSIRIS-REx and Hayabusa2 missions will be similar to CI or CM chondrites or primitive ungrouped chondrites. Samples returned by these missions should preserve an oxidation signature reflective of that found in the local solar nebula during condensation and of changes imparted by aqueous fluids during low temperature parent body processing. This processing results in a distinct distribution of organic functional groups that can be probed using nano-IR, X-ray, and scanning transmission electron microscopy (STEM). We expect these processes to be recorded in samples returned from primitive bodies.

Previous work has established two possible approaches for assessing and tracing the extent of aqueous alteration in primitive meteorite samples: (1) peak splitting of the Fe L-edge to estimate changes in Fe oxidation state across aqueous reaction boundaries and (2) the ratio between oxygen-bearing and non-oxygen-bearing carbon bonding, as observed in the near-edge structure of the C K-edge using soft X-ray absorption spectroscopy (XAS). Both approaches can be performed using either XAS or STEM-electron energy loss spectroscopy (EELS), differing only in scale (few µm2 vs. <1 µm2 analysis areas, respectively). To these techniques, we will add nano-IR spectroscopy, which is sensitive to organic functional group vibrational modes, and synchrotron micro-X-ray fluorescence (XRF), which will allow us to correlate organic speciation with the heterogeneous mineral assemblages and chemical composition found in meteorite and sample matrix. We will apply these correlated measurements to the study of ungrouped and CI and CM chondrites that are spectral analogs for Bennu and Ryugu.

Nano-infrared measurements of these meteorites will enable the VNIR through MIR spectroscopic characterization of matrix phases for which it is difficult or impossible to acquire traditional reflectance or emissivity spectra of pure phases. We will model the optical constants of these phases from their nano-IR spectra, which will

provide an enormous benefit to telescopic and spacecraft spectral studies of primitive small bodies.

To facilitate this work, we propose to purchase a neaspec NeaSNOM near-field infrared system. The instrument will provide near-field imaging and spectroscopy capability over 1.54-15.4 µm, enabling quantitative identification of electronic and vibrational phenomena associated with mineral and organic phases while preserving the nanoscale spatial context of the samples.

This proposal is relevant to the LARS program because we will be develop VNIR and MIR nano-IR hyperspectral imaging and analysis as mature techniques for analysis of returned samples using CI and CM chondrites that are expected to be similar to those returned by OSIRIS-REx and Hayabusa2. The correlated X-ray and TEM analyses will maximize the scientific return of the proposed investigation.

Romy Hanna/University Of Texas, Austin

Multiscale pore characterization and porosity measurement of carbonaceous chondrites in preparation for returned samples from Bennu and Ryugu

Two recent sample return missions, NASA s OSIRIS-REx mission to 101955 Bennu and JAXA s Hayabusa2 mission to 162173 Ryugu, have both revealed a surprising discovery: their carbonaceous chondrite(CC)-type targets are dominated by material with a significantly higher porosity than expected (Rozitis et al, rev. submitted; Okada et al., 2020). Because this porosity (estimated ~30-68%) is significantly higher than CC meteorites, the returned samples are expected to be unlike any CC in our collection, especially in regard to their physical structure and porosity. The origin of this unexpectedly high porosity is not known, but is hypothesized to be original, accretionary microporosity.

We have recently begun development of a technique to characterize the 3D material structure and porosity distribution in CCs using X-ray computed tomography (XCT) and noble gas (Kr, Xe). The highly attenuating gas permeates the sample pores and allows visualization of pores below the resolution of the XCT imaging and quantification of porosity by providing a highly accurate measure of partial porosity (porosity contained within sub-resolution pores). Not only does this technique provide spatial and textural context on the 3D distribution and connectivity of pores, it provides this information within intact samples. It can further be used across spatial scales, interrogating progressively smaller sub-regions in situ. The technique will thus allow characterization of 3D porosity at multiple scales down to sub-µm resolution on cm-sized samples.

The objective of this proposal is to develop the XCT noble gas technique to maturation to accurately characterize and interpret the 3D material structure and porosity, including submicron microporosity, of samples returned from carbonaceous asteroids Ryugu and Bennu. To meet our objective we will build a set of high pressure vessels with PEEK, run extensive XCT tests on three CMs at various scanning conditions, gas species (Kr or Xe) and pressures, and optimize data processing and reduction to derive accurate 3D porosity of the samples. We will then verify the XCT-derived bulk porosity of the samples with

helium pycnometry and investigate the microporosity distribution of select sample areas with (P)FIB-SEM sectioning to validate our XCT-derived microporosity results. We will also investigate how aqueous alteration, impact deformation, and heating within the three CMs have influenced their 3D material structure and porosity distribution in order to better interpret the returned samples.

The proposed work will develop an analytical technique to characterize and measure the 3D material structure and pore network, including submicron porosity, of cm-sized samples of carbonaceous chondrite meteorites, with no sample preparation or cutting necessary. This is a critical analytical capability, which does not currently exist, to address an essential science question regarding the nature of the unexpectedly high microporosity of both Ryugu and Bennu (Okada et al., 2020; Rozitis et al., rev. submitted). Therefore, it will greatly optimize the science return of these two missions, and could be applied to other future sample return missions (Mars sample-return, lunar samples from Artemis or beyond, JAXA s Martian Moons eXploration mission (MMX)) where in-situ, multi-scale characterization of material structure and porosity on undisturbed samples is desired.

Rozitis, B. et al. (rev. submitted) Science Advances
Okada T. et al. (2020) Nature, 579, 518 522

Lindsay Keller/NASA Johnson Space Center
Development of a Next-Generation Scanning-Transmission Electron Microscope and Associated Techniques: Preparing for the Coordinated Analysis of OSIRIS-REx, Hayabusa2, and MMX Samples

We seek funding to acquire a next-generation aberration-corrected field-emission scanning transmission electron microscope (STEM) optimized for atomic-scale imaging and rapid microanalysis of astromaterials. The primary use of this instrument will be to develop and optimize the analytical protocols and techniques that will be required to analyze the primitive carbonaceous materials that will be returned over the coming decade by the OSIRIS-REx, Hayabusa2, and MMX missions. This proposal seeks to take advantage of the transformative developments that have occurred within the last decade in transmission electron microscopy including: high brightness, high stability cold field-emission guns; aberration correction; high-angle annular darkfield imaging; large-area silicon drift detectors (SDDs) for energy-dispersive X-ray (EDX) analysis; and direct-detection cameras for low-dose high-resolution electron energy loss spectroscopy (EELS). The proposed instrument would provide critical sample analysis capabilities that currently do not exist at JSC, and also would be made available to the greater planetary science community. The new instrument and the capabilities it would provide, builds on our long history of innovation and excellence in the coordinated analysis of primitive astromaterials. The proposal team is a diverse, multi-generational collaborative team developing the next-generation STEM for the next-generation of sample scientists.

Bennu and Ryugu, the target asteroids for OSIRIS-REx and Hayabusa2 respectively, are believed to be organic-rich, primitive carbonaceous chondrite-like objects, similar to CI and CM carbonaceous chondrites. Phobos, the target of the MMX Mission, may be a captured C, P or D class water and organic-rich asteroid. The matrices of these materials are dominated by complex, intimate mixtures of minerals and organic matter at the nanometer-scale and pose numerous analytical challenges. The major objective of the proposed instrument is to develop rapid, low-dose, low kV, cryogenic mapping techniques on analog materials that exploit the high X-ray collection efficiency of multiple SD detectors and the newest generation of direct-detection EELS instrumentation. These developments will enable atomic-scale chemical and structural analyses of hydrated and beam sensitive minerals and especially the associated organic matter while avoiding or minimizing the damage to the samples during analysis. Low kV measurements at cryogenic conditions reduce the sensitivity of organic-rich samples to structural damage and mass loss during STEM analysis. These measurements will enable us to determine where insoluble organic matter resides in primitive chondritic materials, its relationship to mineral surfaces, its functional chemistry and isotopic systematics, and to what extent it has been modified by parent body processes. We will coordinate the STEM measurements with nano-IR spectroscopy and soft X-ray absorption near-edge spectroscopy (XANES) data which will provide a unique and complementary dataset. The proposed instrument will enable simultaneous acquisition of EDX and EELS spectrum imaging data resulting in major reductions in the overall analysis time and in electron beam radiation damage to the samples. We have performed several proof-of-concept experiments to support this proposal.

The proposed instrument and technique developments are directly relevant to the goals of the LARS program by providing new capabilities for the nano-scale analysis of astromaterials and by significantly improving the precision and sensitivity of EELS and EDX mapping over the current state-of-the-art. These improvements would result in new information on the chemical and physical processes affecting primitive asteroidal bodies in the solar system and for understanding their origin and evolution.

Ann Nguyen/NASA Johnson Space Center
Investigating the nature of presolar materials and solar system condensates in Stardust samples through coordinated analyses

The isotopic, mineralogical, and chemical study of comet 81P/Wild 2 material returned by the Stardust mission provides unique and surprising insight into the genesis of primordial organics, presolar grains, and nebular condensates and their transport to the outer solar system. The oxygen isotopic compositions of nebular condensates constrain their origins and the oxygen isotopic reservoirs present in the early solar system, but there is a critical need to expand the limited dataset. Evidence of a primordial 16O-poor reservoir has been extremely rare, but materials that originated in the comet forming region should preserve this isotopic signature. In Task 1, we will conduct coordinated mineralogical and O isotopic analyses of early solar system condensates to (a) determine the abundance of 16O-poor materials and address the fundamental question of how many

O reservoirs existed in the early solar system; (b) establish the origins of and relationship between Wild 2, interplanetary dust particle (IDP), and chondrite components; (c) determine the extent of inner disk materials harbored in Wild 2 to understand material transport in the protoplanetary disk.

Comets likely contain the most pristine samples of presolar grains and organic matter (OM) in the solar system because hydrothermal alteration has been minimal on these bodies, in contrast to asteroids. Unlike the well-preserved refractory materials, however, presolar grains and OM were altered to varying degrees or destroyed during the capture process and their nature and abundance in comets remain key questions. Submicrometer-sized presolar grains and OM are likely better preserved among fine-grained material in the bulb regions of aerogel tracks. In Task 2, we will isolate and survey this material for presolar grains to (a) accurately determine their abundance in Wild 2 for comparison with IDPs and chondrites; (b) characterize their mineralogy and chemistry and look for signatures of secondary processing; (c) investigate the injection of supernova material into the solar system. In Task 3, we will determine the molecular-specific distribution and isotopic compositions of OM in the bulb material and in tracks to (a) establish the origin, range and diversity of organic species in Wild 2; (b) characterize refractory CHON particles and nanoglobules.

Approach and Methodology

We will employ our well-developed coordinated analysis approach to characterize the mineralogical, isotopic, and chemical makeup of solar system condensates, presolar grains, and primordial OM in comet Wild 2 samples. Optical/fluorescent imaging, micro-manipulation sample handling, and ultramicrotomy sectioning techniques will be used to document and prepare samples. We will also isolate the substantial, yet largely unstudied, fine-grained bulb material by HF etching of aerogel. The study of fines is vital as they are more representative of the cometary matter and could have originated in the outer solar system. TEM analysis by the JSC and UW groups will identify nebular condensates for coordinated NanoSIMS O isotopic analysis. Most condensates in Wild 2 have small sizes that require analysis by nanoscale techniques such as the NanoSIMS. We will search for presolar grains and anomalous nebular grains in the fine-grained bulb samples by NanoSIMS O, C, N, and Si isotope mapping and conduct coordinated TEM analyses. Organic grains will be measured for their chemical compositions by ¼ L2MS, and H, C, and N isotopic compositions by NanoSIMS. This approach maximizes the scientific information obtainable from Stardust tracks.

Relevance to the LARS Program

This proposal employs a multifaceted approach to the analysis of Stardust mission samples which directly supports the major goals of the LARS program to maximize the science derived from planetary sample-return missions and the Planetary Science Research Program to ascertain the content, origin, and evolution of the solar system .

Erik Oerter/Lawrence Livermore National Laboratory/Dept of Energy
Development of thermogravimetry-enabled laser spectroscopy for the analysis of mineral hydration waters in returned astromaterials

The H and O stable isotope ratios (2H/1H, 17O/16O, 18O/16O) of water and hydroxyl (OH-) in minerals of returned samples from asteroids potentially provide important information about the origin and evolution of the parent asteroids, as well as the origin of water in the early Solar System and the source(s) of water in the terrestrial planets. However, to date it has not been possible to obtain the necessary mineral specific H and O isotope measurements, primarily because of limitations in analytical techniques. Previously available techniques to analyze H isotopes in analogous materials from meteorites suffer from the inability to: (1) analyze separate mineral groups, (2) isolate and analyze organic molecules, and (3) measure the isotopic compositions of H and O preserved in mineral-bound hydroxyl groups in most meteorites.

Lawrence Livermore National Laboratory has recently developed an analytical system that couples a thermogravimetric analyzer with an isotope ratio infrared spectroscopy analyzer (TGA-IRIS) to simultaneously measure a pure or mixed mineral sample for: (1) the bulk H2O/OH- contents, (2) the thermal release profiles of this H2O/OH- to determine the major hydrated minerals present, and (3) the high-precision measurement of mineral-specific H and O isotopic compositions of the H2O/OH- (Oerter et al., 2017, Chemical Geology). Through precise control of sequential step-heating, TGA-IRIS can liberate water from specific mineral types while leaving other mineral groups unaffected. We have conducted preliminary proof-of-concept measurements on a 17mg sample of the carbonaceous chondrite Murchison, as well tests of chemical pretreatments on a series of terrestrial standards. Our preliminary work on the Murchison meteorite indicates that TGA-IRIS can yield 2H/1H, 17O/16O, and 18O/16O data specific to Fe-oxides and phyllosilicates, data which after further development will allow us to evaluate the extent of aqueous alteration that chondritic material such as this has undergone. TGA-IRIS has great potential for adding to our knowledge of the abundances and isotopic compositions of water and organics in returned samples, but the analytical approach needs to be optimized for the unique challenges of complex, fine-grained astromaterials.
We propose a scope of work that will further develop and optimize LLNL s current TGA-IRIS instrument and methodology for returned asteroid samples from the Hyabusa2 and OSIRIS-Rex missions by adding the capability to measure 17O to < 0.2 0, all the while minimizing sample size and maximizing accuracy and precision. The overarching goal of this work is the minimization of sample size requirements, which will be an important aspect for the analysis of returned asteroid samples, and the quantification of precision and accuracy limits for water yield, 2H/1H, 17O/16O, and 18O/16O. We will then test the potential of the astromaterial-optimized TGA-IRIS technique to generate water yield, and H and O isotope data on returned samples by making these measurements on an extensive suite of terrestrial, meteorite and synthetic analogue materials. These measurements will establish the versatility, sensitivity and precision of our technique, and

also provide a more detailed picture of the internal isotopic variability within the meteorites, and thus what might be expected in returned asteroid samples.

Relevance: By developing the unique capability of simultaneously measuring the water abundances, hydrous mineralogy, and H and O isotopes of H2O/OH- in returned samples, this research is directly relevant to the Laboratory Analysis of Returned Samples Program s focus on development of laboratory instrumentation and/or advanced techniques required for the analysis of returned samples . The timeline of our proposed work is perfectly suited to develop TGA-IRIS in preparation for the analysis of samples from the Hyabusa2 and OSIRIS-Rex missions that are due to return samples in 2020 and 2023.

Stephen Sutton/University Of Chicago
Development of XAFS and XRD Methods Applicable to Picogram Samples Returned by NASA Missions Phase 2

The oxidation state and mineralogy of extraterrestrial materials are crucial properties for constraining the conditions under which primitive Solar System objects originated and evolved. This project will develop and test techniques for applying combined synchrotron micro-XAFS (valences and oxybarometry) and micro XRD (mineralogy) methods to picogram mineral grains focusing on FIB methods for producing mono-mineralic samples. Tomographic techniques will be developed to allow the mineralogic information to be visualized in 3D providing the spatial distribution of a selected crystalline or amorphous phase inside these isolated samples and microfragments. The methods will eventually be applicable to returned samples from the Hayabusa2 and OSIRIS-REx missions and ultimately for returned Martian samples. This proposal is a successor to award 80NSSC18K0500.
We have successfully developed Phase-1 sample preparation and analysis methods. For micro-XAFS of FIB sections, we weld the FIB section to copper lift-out grids. For micro-XRD tomography, microfragments are mounted to fiber tips which in turn are held in a Huber goniometer head coupled to a rotation stage. By comparing the FIB valence results with associated results obtained in thin section pre-FIB, we have demonstrated that the ion beam milling has negligible effects on the XAFS spectra and resulting inferred valences for Ti, V, and Cr. In addition, as return sample analogs, olivine and pyroxene FIB sections from two Antarctic micrometeorites were successfully analyzed by Ti, V, and Cr micro-XAFS. We have also demonstrated that tomographic slices of XRD data can be collected at frame rates faster than 50 ms per pixel while maintaining excellent signal to noise and good reconstructions.
In Phase-II of this project, additional work will be done to alleviate and test some of the shortcomings of the current methodology. First, the current FIB mounting scheme allows rotations of only ±30° because of obscurations by the grid. We will develop an improved mounting scheme (pin-type) to allow full 360° analysis of the FIB sections, essential for tomography and accurate corrections of the micro-XAFS data for orientation effects. Second, the tomographic XRD methods will be improved to minimize artifacts and advance analysis of single-crystal and powder-like diffraction from picogram multiphase samples.