Laboratory Analysis of Returned Sample
Abstracts of Selected Proposals
(NNH17ZDA001N-LARS)

Below are the abstracts of proposals selected for funding for the LARS program. Principal Investigator (PI) name, institution, and proposal title are also included. 22 proposals were received in response to this opportunity. On January 10, 2018, 6 proposals were selected for funding.

Jamie Elsila/NASA Goddard Space Flight Center
Developing An Efficient Coordinated Organic Analysis for Returned Samples

Objective: To develop an efficient protocol for the coordinated analysis of soluble organic compounds in a returned sample while maximizing the breadth of compounds analyzed with minimal bias and contamination for limited sample size.

Background: Sample extraction and workup has been called a forgotten art. Efforts to increase the efficiency and efficacy of the essential steps that extract and purify organic compounds in complex samples have not kept pace with improvements to instrument sensitivity. Yet these preparative steps are when the sample has the greatest risk of contamination and loss. A rigorous analysis of the trade-offs that bias yields of one compound class, let alone many, is rarely performed; thus, current coordinated analysis techniques may be flawed. Upcoming sample return missions will require an unbiased extraction of a wide distribution of compound classes for small samples.

There is a large database of analyses of soluble extraterrestrial organic compounds in meteorites, lunar samples, and other samples relevant for comparison with the asteroidal material to be returned by Hayabusa2 and OSIRIS-REx. However, many of these studies focus on individual compound classes (e.g., amino acids, PAHs, carboxylic acids, amines) to answer specific questions, treating the samples in ways to maximize data return from one compound class at the expense of others. In addition, different techniques have been used for the same compound classes, and the systematic biases (e.g asymmetric compound losses, decomposition, isotopic fractionation) introduced by many of these methods are unreported. Scientific interest in returned samples extends to understanding the broader inventory of soluble organics and how abundances, distributions, and isotopic compositions of different compounds may be correlated. The limited sample sizes and precious nature of returned samples means that performing parallel extractions optimized for each compound class is wasteful.

We propose to evaluate and optimize methods to create an efficient coordinated sample extraction and purification protocol that enables analysis of multiple soluble organic compound groups, maximizes efficiency of sample use, and allows for meaningful comparison of this data with previous measurements. We will produce a roadmap that details and assesses the trade-offs and decision points to be considered in future analyses of returned samples.

Methodology: We will use a series of standards representing a wide range of meteoritic soluble organic compounds (e.g., amino acids, amines, carboxylic acids, hydroxy acids, aldehydes, ketones) along with samples of the Murchison meteorite. We will begin by optimizing purification methods, then proceed to hydrolysis and extraction. We will start with methods previously described in the literature and modify conditions (e.g., solvents, temperature, times, pH, etc.), analyzing the resulting fractions to note effects on the yield, relative distributions, and isotopic compositions of the standards.

Relevance: The proposed work develops "new analytical techniques for existing instrumentation that will push the limits of current technology as described in the LARS call. These new techniques will maximize analytical potential by focusing on efficient extraction and purification of soluble organic compounds in rare samples. The protocols developed will be aimed at future analyses of Hayabusa2 and OSIRIS-REx material.

Christine Floss/Washington University
Complementary Micro-Analytical Investigations of Comet 81P/Wild 2 Samples Returned by NASA s Stardust Mission

Sample return space missions provide us with the opportunity to directly analyze materials that would not otherwise be available for laboratory analysis. By studying such samples with an array of complementary analytical techniques, it is possible to obtain comprehensive isotopic, compositional and mineralogical information that can then be interpreted within an astrophysical or cosmochemical context. The Stardust mission to comet Wild 2 has provided a wealth of information about the building blocks comprising cometary material and has revised our understanding of the evolution of the solar system. Here we propose a multi-pronged analytical approach, building on our earlier studies, to further advance our understanding of these samples and the outer nebular environment in which they resided. Our work will focus on studying samples from Wild 2 with a combination of SEM, NanoSIMS, Auger spectroscopy and FIB-TEM. We will also investigate experimental analog materials and hypervelocity impact test shots for comparison purposes, in order to aid in the interpretation of Wild 2 data.
The proposal team will consist of PI Christine Floss and Co-I Keven Croat, both at Washington University in St. Louis. Funding will be requested for a graduate student, who will spend the bulk of his or her thesis work on projects carried out under this proposal. Partial funding will also be requested for an undergraduate student, whose task it will be to assist with the routine documentation and characterization of impact features on the Al foil samples. PI Floss will be in charge of the overall management of the project and will be directly involved in most of the proposed elemental and isotopic analytical work. Co-I Croat will carry out much of the FIB-TEM work proposed herein. Both Floss and Croat will be responsible for training the graduate student and overseeing his/her work. Mark Burchell and Anton Kearsley, associated with the University of Kent, will serve as collaborators on this project. Both have contributed samples of hypervelocity impact experiments and, through their extensive experience with such studies, will help with the interpretation of the results. Finally, collaborator Alian Wang,

at Washington University in St. Louis, will carry out the Raman imaging of selected craters and will assist with interpretation of the results.
The comprehensive analyses of samples from Stardust proposed here address the core goals of the LARS (Laboratory Analysis of Returned Samples) program to maximize the science derived from planetary sample-return missions, as outlined in the ROSES 2017 NRA. Our research aims to address fundamental questions about the nature of the returned extraterrestrial material and its state of preservation, and to use that information to provide constraints on grain formation and early solar system evolution. Through its relevance to the LARS program, it is also relevant to NASA s Strategic Plan to ascertain the content, origin, and evolution of the Solar System.

Gary Huss/University of Hawaii, Honolulu
Isotopic investigation of cometary particles returned by the Stardust Mission from comet Wild2

This proposal describes a program to continue isotopic measurements of Stardust cometary particles. The goal of this research is to understand the constituents and makeup of comet Wild 2 and to use the information to understand how this and other comets formed, leading to a better understanding of the origin of the solar system. This work is part of a consortium study of the chemistry, mineralogy, petrology, and isotopic compositions of comet Wild 2 samples. This effort combines skills and tools available to Andrew Westphal s group at the University of California at Berkeley, consisting of Dr. Westphal, Anna Butterworth, Zack Gainsforth, and Christine Jilly-Rehak, and those of Dr. Gary Huss and his colleagues, David Frank and Kazu Nagashima, at the University of Hawai i (UH). Hope Ishii and John Bradley, who operate the Advanced Analytical Electron Microscopy Center, will also work with us. They have a Titan superSTEM (scanning transmission electron microscope) and Helios Dual-Beam focused ion beam (FIB) instrument that can be used in this research. Ryan Ogliore, now at Washington University, St. Louis, is also a collaborator.

Our research program will dramatically increase the number of fully characterized large terminal particles that have been measured for oxygen isotopes. This will permit us to test hypotheses about the source(s) of the high-temperature mineral grains, chondrule fragments, and CAI fragments that have been discovered in the Wild 2 samples. We will also investigate the chronology of these larger particles using the 26Al-26Mg and 53Mn-53Cr chronometers. Current data suggest that the chondrule and CAI fragments found in Wild 2 formed relatively late, a few million years after the formation of the first solar system solids. But the data are limited, and identification of early-formed objects among the samples would significantly change the way we currently think about the constituents of Wild 2.

We will continue to investigate the sulfur isotopic composition of suitable particles to learn about how the sulfur-rich particles formed and how they relate to sulfides and other sulfur-rich materials from the inner solar system. We will intensively study any presolar grains that are identified in the course of this work. In addition to measuring their isotopic compositions, we will study presolar grains and other especially interesting grains with

the Titan superSTEM. Studies of chondritic porous interplanetary dust particles (IDP) will be carried out to provide context for interpreting the Wild 2 samples.

The goal of the LARS program is to maximize the science derived from planetary sample-return missions. This project is designed to do this for the Stardust samples; the Stardust Mission is explicitly called out in the program AO. Our consortium approach and state-of-the-art equipment permit us to get the maximum return from each sample studied. At the end of this project, we will all have a better understanding of comet Wild 2, its constituents, and the processes involved in the formation of the solar system.

James Lyons/Arizona State University
Ion microprobe analysis of LDEF Al targets to determine oxygen isotope composition of Earth upper atmosphere, and comparison to MAVEN

NASA Laboratory Analysis of Returned Samples Step 1 proposal (2017)

Title: Ion microprobe analysis of LDEF Al targets to determine oxygen isotope composition of Earth upper atmosphere, and comparison to MAVEN

PI: James Lyons, ASU; Collaborators: Kevin McKeegan, Ming-Chang Liu, UCLA

Introduction: The Long Duration Exposure Facility (LDEF) was launched into low Earth orbit in 1984, and retrieved in 1990 by Columbia. The original orbit was at 480 km, but over the course of the (unplanned) extended mission, the orbit decayed to 330 km. A suite of targets were placed at various locations on LDEF to assess and collect impacting IDPs. In addition to collecting IDPs, targets on the leading edge of the spacecraft also impacted Earth s upper atmosphere at an orbital velocity ~ 8 km s-1. Here we propose to use depth profiling by ion microprobe to measure the oxygen isotope composition of Earth s upper atmosphere. The oxygen composition of the upper atmosphere is primarily O atoms and O+ ions. These highly reactive species become implanted in the target surface and apparently replace O in the anodized target oxide layer present at launch. Our first set of measurements on 3 LDEF Al targets with the Cameca 1290 at UCLA has shown a peak isotope depletion of d18O ~ -200 0, but these measurements were made without a proper standard. We have also shown that no appreciable O isotope signature is present in Au and Ge LDEF samples. Here we propose a systematic exploration of Al targets from LDEF, including the use of proper standards. We will use SRIM (Stoppage and Range of Ions in Matter) software to model implantation of O atoms into the Al oxide layer, and to simulate ion-beam mixing of surface O atoms to deeper levels in the oxide. This modeling will allow us to better determine the true upper atmosphere O isotope composition. In addition to determining the oxygen isotope composition of Earth s upper atmosphere, the analyses proposed here offer the possibility of a direct comparison of Earth upper atmospheric oxygen isotopes to very recent measurements made by MAVEN for the Martian upper atmosphere.

Proposed research:

1. Ion microprobe measurements of O isotopes from LDEF Al targets. We will measure d17O and d18O on 3 sets of Al LDEF targets: i) ~10 targets from D. Humes experiment (LDEF S0001), together with an unflown piece of identical Al (from D. Humes); ii) several targets from F. Horz experiment (LDEF A0187-1), using the backside of a target as a standard; 3) several samples of LDEF Al support structure (so-called intercostals), again using backside as a standard. The intercostals sample all locations on the spacecraft.
2. SRIM code modeling of O ion implantation into Al oxide layer. We will use the SRIM code (freeware available from J. F. Ziegler) to calculate the penetration of O atoms of known kinetic energy into an LDEF Al target, and to calculate mixing effects due to the ion microprobe Cs+ ion beam, allowing us to determine the peak depletion of d18O.
3. Modeling of results and implications for Mars. Although the focus of this proposal is on the measurements from the LDEF targets, and on the SRIM modeling, we will interpret the results using an atmospheric model that includes diffusive separation, and we will apply the results to a similar model for Mars for comparison with eventual MAVEN data.

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

The oxidation state and mineralogy of extraterrestrial materials are crucial properties for constraining the conditions under which primitive Solar System objects originated and evolved. Synchrotron-based x-ray absorption fine structure (XAFS) techniques have proven to be valuable in defining oxidation state where the valences of multivalent elements (Ti, V, Cr, and Fe) are used as proxies. Coupled with high-speed, synchrotron x-ray microdiffraction (micro-XRD) mapping, new opportunities are available to correlate chemical state and mineralogy (including orientation and strain) at micrometer scales. These methods have been applied to relatively large (> tens of μm) mineral grains and glasses in thin sections. However, samples returned by NASA spacecraft are typically characterized by mineral grains of much smaller dimensions (<10 μm). The proposed work will develop and test techniques for applying micro-XAFS and micro XRD 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 picogram samples, ideally within sealed containers and capture media without the need for extraction. The methods will be applied to Stardust grains from comet Wild-2 and Hayabusa1 grains from asteroid Itokawa and will be applicable to returned regolith samples from the Hayabusa-2 and OSIRIS-Rex missions.

We will develop and test micro-XAFS and XRD techniques applicable to picogram extraterrestrial samples using the GSECARS x-ray microprobe at the Advanced Photon Source. For focus of micro-XAFS studies will be using FIB methods to produce mono-mineralic samples. Development will be accomplished using valence state standards (both minerals and glasses). FIB sections will also be made of larger mineral grains from

meteoritic thin sections where XAFS spectra for the FIB sample and parent grain in thin section can be used to test for valence alterations due to sample preparation. Micro-XRD studies will also utilize these FIB sections, but the ultimate goal will be to develop methodologies for samples that are mineralogically heterogeneous at the micrometer scale. A new generation of high speed area detectors will be used to collect the diffraction data in mapping mode with accumulation times <100 msec per pixel. Interpretable diffraction patterns will be collectable from picogram samples/voxels. We will develop methods to collect the data tomographically and reconstruction algorithms to visualize the diffraction pattern within reconstructed slices of the analyzed materials. These methods will then be applied to Stardust mineral grains, notably from olivine- and pyroxene-bearing tracks. The coupled XAFS/XRD data may also be useful in identifying materials produced/modified during capture.

This work will develop coordinated valence/oxidation state and mineral phase determination methods applicable to picogram samples returned by NASA missions and will provide insights into the origins of sampled Solar System bodies. The results will also likely provide insights into the redox effects and mineral modifications of secondary processes, such as re-melting, shock and capture. Thus, this study is relevant to the call of the Laboratory Analysis of Returned Samples (LARS) program element.

Roger Wiens/Los Alamos National Security, LLC
GENESIS Mission Constraints on Solar-Wind Fractionation: CNO Regime Measurements and Data Analyses to Determine Solar Abundances from the Solar-Wind

. The original solar isotopic and elemental abundances constitute an important reference point from which all other solar-system compositions can be compared. The overall goal of the GENESIS solar-wind sample return mission was to provide this compositional database. However, in order to determine solar compositions from solar wind, the latter must be corrected for fractionation, which occurs both for isotope ratios and elemental abundances. Some progress has been made in constraining the first-ionization potential (FIP) fractionation that characterizes elemental abundances, but there is as yet no comprehensive theory that explains this fractionation and, more importantly, extends to predicting the correct isotopic fractionation.
. A key piece of information is that the Sun produces different types, or regimes, of solar wind which differ in their fractionation. The fast solar wind is less fractionated than other wind regimes and may be close to the actual solar composition. GENESIS provided samples of each of the three solar-wind regimes. Regime-specific samples have been analyzed for light noble gases (He, Ne, Ar) and are being analyzed for several low-FIP elements. However, key elements of intermediate FIP C, N, and O have not yet been analyzed. These elements are critically important, as they bound the transition between low-FIP and high-FIP fractionations a key piece of evidence to match to solar-wind fractionation theory. We propose to analyze these elemental abundances in regime-specific samples using an ion probe. We will use the back-thinning sample technique successfully applied for analysis of several other elements in GENESIS samples. This allows the ion probe to begin its profile from the back of the implant region, in an area

free of surface contamination, avoiding driving surface contaminants farther into the implant region.

. To support these measurements, we propose to provide comparisons with elemental compositions provided by the Ulysses SWICS instrument across several solar cycles to understand the long-term stability of solar-wind compositions. This follows an important discovery we made with ACE SWICS data showing for the first time that the velocity-dependent component of the solar wind is mass fractionated. The newly re-calibrated Ulysses data provides a much longer time window to study this and related phenomena that are critical to placing the Genesis measurements in their proper context.

. This proposal responds in the broadest sense to the LARS goal, which is to maximize the scientific return from the samples provided by &GENESIS . We propose to perform critical sample analyses identified among the top 4 analytical objectives of the GENESIS mission, and support these measurements with a broader study to place all GENESIS sample measurements in their proper context from which solar isotopic and elemental abundances can be determined.