Laboratory Analysis of Returned Samples
Abstracts of Selected Proposals
(NNH16ZDA001N-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. **29** proposals were received in response to this opportunity. On December 16, 2016, **12** proposals were selected for funding.

Donald Burnett/California Institute of Technology
Genesis Samples: Analysis and Technical Enabling

This proposal requests funds to extend: (II) secondary ion mass spectrometry (SIMS) analysis of Genesis samples, and (III) our work expediting Genesis science which we refer to as Technical Enabling: (A) Aiding the work of other Genesis PIs (e.g., providing and calibrating implant standards), (B) Developing techniques to remove crash-derived surface contamination and (C) Science Co-ordination, most importantly interacting with the solar physics community. (Headings from proposal text)

Genesis provides precise isotopic and elemental abundances, but fractionations between the Sun and the solar wind (SW) must be evaluated. Elemental fractionations appear to be correlated with first ionization potential (FIP). Spacecraft data indicate elements with FIP<9eV (much of the periodic table) are unfractionated. Genesis data check this with higher accuracy.

II. Specific analysis projects which we lead: (C) Fe, Mg. These are abundant elements which serve as reference elements for other Genesis elemental analysis and must be measured to the highest possible accuracy. Final Fe and Mg fluences are available. (D) Na, K. These are among the lowest FIP elements, thus critical in determining the extent of FIP fractionation. (E) Mg isotopes in diamond-like-C collectors. Genesis data demonstrate isotopic fractionation between the solar wind and Sun, but do not provide quantitative estimates; these are possible with Mg isotopes. (F) Comparison of solar Cs abundance with predictions from s- and r-process nucleosynthesis constrains ion-neutral chemical fractionation during the formation of the solar system. (G) Ca/Al abundance. Backside depth profiling techniques have been used to avoid serious surface contamination problems for this important ratio. (H) Fe/Mg in SW regimes; ACE spacecraft data predict differences. (I) Mn fluence, checking large difference between CI and photosphere. (J) Rb fluence. In addition to being an important low FIP element, the combination of Genesis Rb and Kr fluences provides a constraint on possible gas/solid fractionation between the Sun and the solar nebula.

IIIA Collaborations with other PIs: (a) H fluence with G Huss. Data show less FIP fractionation in highs speed SW relative to bulk. (b) Ni fluence with synchrotron radiation grazing incidence X-ray fluorescence with M. Schmeling. Preliminary data

suggest a significantly higher Ni fluence than expected. (c) Br fluence with A. Meshik. (d) Cl, Co, and Ir fluences with K. Nishiizumi. As siderophile elements, Ni, Co, and Ir provide a possible constraint on metal/silicate fractionations in the solar nebula. Co and Ir are siderophile elements differing greatly in mass, which by comparison with CI abundances, constrains the possibility of heavy element gravitational settling out of the solar convection zone. (e) Sr, Se fluences with I. Veryovkin. As with Rb and Br, data for elements in the mass 80-90 range provide a constraint on possible gas/solid fractionation between the Sun and the solar nebula. (f) Regime analysis of CNO (with Wiens) tests theories of FIP fractionation. (g) Re and Os isotopes (with Sharma).

IIIB Meeting Genesis science objectives requires analyses of large (100 mm2) area samples. In collaboration with the Genesis Curatorial Facility and other PIs, we are developing techniques to remove crash-derived particulate contamination. Focused studies on specific Si samples will be finished, then work will begin on diamond-like-C (DLC) and sapphire collector materials, especially the Concentrator DLC sample for which bare Si areas should permit C isotope measurements.

IIIC At our request, data from the ACE spacecraft have been reprocessed to give more accurate abundances, and new theories for FIP fractionation are being developed.

Michael Callahan/Boise State University
Developing Next Generation Techniques for the Comprehensive Analysis of Organics in Returned Samples

We propose to develop next generation techniques for the comprehensive analysis of organics in returned samples. We will develop novel extraction methods and use a combination of state-of-the-art high resolution mass spectrometry and ultrahigh performance nanoliquid chromatography-high resolution mass spectrometry (Callahan et al. 2011 and 2014) for targeted and untargeted analyses of organic compounds. We will design these analytical techniques towards the analyses of organics in samples that are micron-sized and weigh in the nanogram range. These analytical techniques will be particularly beneficial for returned samples with finite amounts and extremely limited sample size because these samples are highly challenging to analyze, the organics are usually in trace amounts, and few techniques can provide analyses of organics at the full molecular level.

In addition to the development of analytical methods and techniques, we will analyze cometary particles and grain tracks in aerogels from the Stardust mission as another primary goal. We will also incorporate a novel analytical strategy called meteoromics, which includes high-level data analyses, to compare organics in cometary samples to other extraterrestrial materials such as carbonaceous meteorites. Our state-of-the-art analyses of cometary particles and grain tracks in aerogels would significantly advance our understanding of [1] complex organics in comets, [2] the distribution of complex organics in the Solar System (particularly the outer Solar System), and [3] their potential role in the origin of life on Earth, which would maximize the science derived from the Stardust mission.

The proposed research is within the scope of the LARS program because developing next generation analytical techniques for a comprehensive molecular-level analysis of Stardust returned samples is directly relevant to the two activities supported by the LARS program, namely [1] development of laboratory advanced techniques required for the analysis of returned samples and [2] direct analysis of samples already returned to Earth. The analytical techniques that we propose to develop and utilize are not limited to the Stardust returned samples only. They would be highly valuable towards the analysis of organic composition in highly sample-limited returned samples such as Hayabusa1 and Hayabusa2 and future returned samples from OSIRIS-REx; this is especially true considering their asteroidal origin and our ability to compare these samples with our existing database of meteoritic organics.

Nicolas Dauphas/University Of Chicago
Development of a novel chromatography system for the analysis of returned samples

Objectives:

In September 2016, NASA will launch a rocket to send the OSIRIS-REx spacecraft on a rendez-vous mission to B-type asteroid 101955 Bennu for sampling its surface. Much of the discussion on these rocks will undoubtedly involve understanding their irradiation history. For how long were the rocks exposed to galactic cosmic rays? At what depth were the rocks buried when they were exposed to those cosmic rays? Did such irradiation affect the chemical and isotopic compositions of the rocks and if yes, can such effects be corrected for? How are cosmogenic effects affected by the target composition and its water content? The best tracers of those effects are isotopes with large capture cross sections and resonance integrals for thermal and epithermal neutrons. Lanthanides (REEs) possess many isotopes with large thermal neutron cross sections and resonance integrals. They have proven to be extremely useful for understanding the cosmic ray exposure history of lunar rocks and meteorites. Given that OSIRIS-REx will recover surface asteroidal samples, consideration of those effects will be important.

There is little expertise in the USA on calculation of neutron capture effects in REEs and much of the focus in REE isotope measurements has been in the analysis of Sm and Nd for geochronologic applications. The proposed work will allow us to (1) continue developing and testing ChRobot, a new automated chromatography system for purifying REEs to measure neutron capture effects, (2) document cosmogenic effects for REEs in targets of carbonaceous chondrite compositions, for which almost no data is available, and (3) develop the scientific context for interpreting those variations by running simulations of neutron capture effects in target compositions representative of the materials that OSIRIS-REx may encounter.

Methodology:

Over the past 2 years, we have developed an all-teflon pneumatic chromatography system to separate REEs from one another. The motivations for developing this system are two-fold: (1) it allows us to isolate elements that are notoriously difficult to separate from one another by running longer columns under controlled temperature conditions, yielding better chromatographic separations, and (2) it allows us to achieve better separations in a computer controlled procedure, using less column passes, thus minimizing the risk of sample loss, contamination, and mishandling. More elements can be separated in a single column pass, making optimum use of the samples.

The system is established and the next 3 years will be devoted to assessing its routine operation to separate REEs for study of neutron-capture effects. Scientifically, we will address the question of how do different target materials and secondary energy spectra affect the isotopic compositions of the REEs? This will be investigated by (1) combining isotopic analyses of elements that have different sensitivities to different neutron energies and (2) studying those effects in carbonaceous chondrites, taken as proxies for Bennu samples. Those measurements will be combined with ongoing simulations of neutron capture effects in an inversion calculation to derive the secondary neutron energy spectrum. The calculations will investigate how target compositions (e.g., variable water contents) affect cosmogenic effects for the REEs.

Relevance:

This study will strengthen the expertise of a US lab in the measurements and interpretation of cosmogenic neutron capture effects in planetary surfaces of carbonaceous chondrite compositions, a key aspect of the study of the OSIRIS-REx mission. It is thus highly relevant to NASA s strategic objectives (solicitation NNH16ZDA001N-LARS), which include Development of laboratory instrumentation and/or advanced techniques required for the analysis of returned samples (document C18 of the solicitation, page C.18-1).

Andrew Davis/University Of Chicago
Isotopic and chemical analysis of cometary, interstellar, and asteroidal dust and solar wind with CHILI

Science Goals and Objectives. The general themes are to study the chronology of cometary and asteroidal dust, nucleosynthetic isotopic anomalies in cometary and interstellar dust, and elemental abundances in and acceleration mechanisms of the solar wind. Measurements of chemical and isotopic compositions of samples returned to Earth by the Stardust (1,2), Genesis (3), and Hayabusa (4) missions, will be done using CHILI, a resonance ionization mass spectrometer. (1) Much is now known about the mineralogy, mineral chemistry, and textures of dust from comet Wild 2, and some measurements of O and Mg isotopic composition are available. We plan to improve knowledge of the Stardust cometary samples by: (a) 26Al-26Mg chronology of Al-rich phases in chondrule-like and CAI-like objects, which are currently limited by spatial resolution and sensitivity; and (b) searches for isotopic anomalies in Ti, Fe, Ni, Sr, Zr, Mo, and Ba, which have not been possible to date. (2) The most challenging of all extraterrestrial

samples are candidate particles identified by the Stardust Interstellar Preliminary Examination team. Are they really interstellar? Are they pristine circumstellar condensates? Have they been significantly processed in the interstellar medium? We will measure the isotopic compositions of Mg, Si, Ti, Fe, and Ni, allowing recognition of nucleosynthetic anomalies and inferences about their presolar history. (3) One of the primary goals of the Genesis mission is to better determine solar abundances of the elements, for which the acceleration mechanism of the solar wind must be well characterized and understood. Abundances relative the photosphere measured for Genesis samples for elements with first ionization potentials (FIP) <10 eV are constant, whereas those with FIP >10 eV drop with increasing FIP. However, few elements with FIP <10 eV have been measured: only Na, Mg, Al, Ca, Cr and Fe, and even these data have not been published in the refereed literature. We will significantly expand this list, by analyzing Ti, Mn, and Ni as well as the heavy elements with the highest cosmic abundances, including Sr, Y, Zr, Mo, Ba, Ce, Nd, Gd, and Pb. (4) Samples of asteroid Itokawa returned by the Hayabusa spacecraft most closely resemble equilibrated LL chondrites. We plan to study the chronology of Hayabusa particles by analyzing fine-grained plagioclase for 26Al-26Mg with CHILI, and if high Hf/W phases can be found, study the 182Hf-182W system.

Methodology. CHILI, the CHicago Instrument for Laser Ionization, is now operational and has recently measured Fe, Ni, Sr, Zr, and Ba isotopic compositions of presolar SiC. CHILI represents a significant advance beyond the current state-of-the-art for in situ isotopic and chemical analysis, with a lateral resolution as small as 10 nm, a useful yield (atoms detected per atom desorbed) of 30 50%, and nearly complete suppression of isobaric interferences from both monatomic and molecular ions. Many of the tasks can be done with CHILI as it works today, but others, such as achieving the finest lateral resolution and developing three dimensional isotopic image reconstruction will require further development of software, but with minor hardware upgrades. Also available are a TESCAN LYRA3 FIB/FESEM equipped with dual SDD detectors, WDS, and EBSD. Characterization of samples by synchrotron and SIMS methods by collaborators will complement this work.

Relevance. The proposed research is highly relevant to the goals of the Laboratory Analysis of Returned Samples program, which is targeted at building and developing advanced instrumentation for analysis of returned samples from the Genesis, Stardust, and Hayabusa missions as well as studies of those samples with existing instrumentation. We propose some further instrument development and a significant program of sample analysis.

John Eiler/California Institute of Technology

Isotope Ratio Fourier Transform Mass Spectrometry: A Novel Technology to Measure Isotopic Structures of Organic Molecules Returned from OSIRIS-REx

The OSIRIS-REx mission is expected to return to earth 60+g of material sampled from the asteroid Bennu. This body has spectral properties resembling the inferred parent bodies of classes of meteorites that are rich in volatiles, including organic compounds.

This mission will provide a rare opportunity to explore the organic chemistry of a solar system body outside the Earth where the source and environmental context of the sample is well known, terrestrial contamination is minimal, and there is relatively abundant material for laboratory study. Stable isotope compositions (D, 13C, 15N, 17,18O, 33,34,36S) of meteoritic, nebular and interstellar organics record their precursors and formation mechanisms; therefore stable isotope measurement technologies appropriate for organic molecules will be key to the study of samples returned by OSIRIS-REx.
We propose to develop technology and methods for the analysis of stable isotope distributions in organic compounds returned from Bennu, including: (1) bulk stable isotope contents of individual molecules (i.e., averaged across all atomic sites in that molecule); (2) position-specific differences in isotopic content between non-equivalent atomic sites in a given molecule; and (3) proportions of multiply-substituted isotopologues (i.e., versions of the analyzed molecule containing two or more rare isotopes).

We will accomplish this using Fourier-transform mass spectrometry (FTMS), which has extraordinary mass resolution (M/ M ~105-106) and the capacity to make measurements across large ranges of mass, on many peaks per compound. We will adapt for this purpose the Q Exactive GC (QEGC), an instrument produced by Thermo Fisher Scientific. The QEGC has an electron impact gas ion source, quadrupole for mass window selection, collision cell for MS-MS experiments and, most importantly, contains an Orbitrap (compact electrostatic FTMS). The central idea behind our approach is to ionize each organic molecule by electron impact, producing a mass spectrum containing numerous peaks that each sub-sample the molecular structure in different ways (thus encoding position specific isotopic information). Portions of that mass spectrum that are known to contain molecular sites of interest (or to sample the molecule as a whole) will be selected using the quadrupole and passed to the Orbitrap for isotope ratio analysis, including both singly and multiply substituted species. We present a pilot study documenting the ability of this machine to return isotope ratios with precisions in the range 0.2-1 0, to be similarly accurate when appropriately standardized, and to recover known isotopic contents of portions of organic compounds.
Our work on the QEGC will focus on: (1) fundamental characterization of its performance as a mass analyzer (e.g., limits of precision and sensitivity); (2) development of methods of sample introduction optimized for analysis of trace organics; and (3) proof of concept studies of organics extracted from the Murchison meteorite. We will focus on the amino acids, which are important constituents of extra-terrestrial organic matter and have been the subject of many previous studies. However, the instruments and methods should be generalizable to other classes of organic molecules.
This proposal is a collaboration between two groups with complementary prior experience: PI Eiler will provide expertise and instrumentation for analysis of isotopic structures of molcules; Co-I Elsila will provide expertise in the extraction, purification and derivatization of amino acids from meteorites, and in the application of stable isotope geochemistry to organic cosmochemistry.

Christine Floss/Washington University
Identification and Analysis of Impact Craters on Al Foils from the Stardust Interstellar Collector Tray

In addition to the first unambiguous cometary samples from comet 81P/Wild 2, NASA s Stardust mission was designed to collect the first samples of contemporary interstellar dust. The Stardust interstellar dust collector collected particles for 195 days during two exposures prior to the spacecraft encounter with Wild 2 and tracked the interstellar dust stream for all but 34 days of that time. The initial investigation of these samples took place under the auspices of the CAPTEM-approved Stardust Interstellar Preliminary Examination (ISPE) and resulted in the discovery and characterization of seven probable interstellar dust particles, four of which were identified from impact craters in the Al foil. We propose to continue to carry out searches for impact craters in Al foils removed from the Stardust interstellar tray. The dust particles are estimated to be in the picogram to 100 femtogram mass range, roughly three orders of magnitude smaller than the typical nanogram cometary dust particles, and their fluence is about two orders of magnitude smaller than that of the cometary particles.
Our crater searches are carried out using automated high-resolution secondary electron (SE) mapping of aluminum foils followed by manual examination of images to locate potential craters. Image examination will take place via a modified Stardust@home project in which citizen scientists search for craters in the foils via an online virtual microscope . Craters identified in this manner will be analyzed by Auger spectroscopy to non-destructively determine major element compositions and to evaluate whether residues are consistent with extraterrestrial materials or contain diagnostic signatures from secondary spacecraft ejecta.

The proposal team will consist of PI Christine Floss, at Washington University in St. Louis, and collaborator Andrew Westphal, at the University of California, Berkeley. PI Floss will be responsible for the overall direction of the project and will carry out all of the SEM scanning of the foils, as well as Auger analyses of the impact residues in the craters. Co-I Westphal developed Stardust@home and will be responsible for uploading the foil images and managing the identification of craters via this citizen scientist project. Through the search for and identification of rare impact craters from the Stardust Interstellar Dust Collector, this research supports the goals of NASA s Laboratory Analysis of Returned Samples Program to maximize the science derived from planetary sample-return missions, as outlined in the ROSES 2016 NRA. Precisely because so few interstellar dust impacts are expected, it is critical to locate and analyze as many of them as possible. Comparison of the properties and compositions of contemporary interstellar dust with other presolar and solar system materials provides information on the evolution of the local environment from which our sun and planets originated and thereby supports the goals of NASA s Planetary Science Research Program to help ascertain the content, origin, and evolution of the Solar System.

Evan Groopman/Naval Research Laboratory

Fe and Ni measurements of Genesis Solar Wind collectors by Secondary Ion Accelerator Mass Spectrometry

The objectives of this proposal are the measurement by Secondary Ion Accelerator Mass Spectrometry of the Fe and Ni elemental abundances and isotopic compositions in Genesis Solar Wind (SW) collectors, and the calculation of SW elemental and isotopic fractionation based upon these measurements. These measurements address revised Genesis Mission objectives described by Burnett and Jurewicz (The Future of Genesis Science: A Special Report to NASA by D.S. Burnett & A.J.G. Jurewicz), specifically, Science and Measurement Objectives # s 2 and 3: (2) Science Objective: Measure average solar nebula composition for elements having low first ionization potential. These are the rock-forming elements which make up the terrestrial planets. Measurement Objective: Abundances of elements with low first ionization potential ; (3) Science Objective: Test for systematic differences in isotopic compositions between Sun and planetary materials. Measurement Objective: Isotopic compositions of non-volatile elements heavier than Ar, specifically Fe. This proposal aims to satisfy the objectives of the Laboratory Analysis of Returned Samples (LARS) program, which seeks to maximize the science derived from planetary sample-return missions, including Genesis. This proposal will utilize new instrumentation and measurement techniques, namely the world-unique Secondary Ion Mass Spectrometer Single-Stage Acceleration Mass Spectrometer (SIMS-SSAMS) at the U.S. Naval Research Laboratory (NRL) in Washington, DC, which will augment the measurement capabilities available at other laboratories investigating Genesis SW samples. The NRL SIMS-SSAMS is a sibling of the UCLA MegaSIMS. These instruments differ meaningfully, however, in the type of accelerator they employ the SIMS-SSAMS uses a single-stage accelerator, while the MegaSIMS uses a traditional, tandem accelerator. The SIMS-SSAMS single-stage accelerator allows it to accept either positive or negative secondary ions from the SIMS frontend, allowing for the analysis of nearly the entire periodic table with the accelerator and ideal for measurements of Fe, Ni, and many of the elements addressed by the remaining Genesis Science Objectives. The most important drawbacks of SIMS alone are the low useful ion yields from the sputtering process, typically < 1%, and the generation of secondary molecular ions, which can isobarically interfere with masses of interest. AMS excels at separating atomic and molecular isobaric signals. The NRL SIMS-SSAMS removes the drawbacks of both techniques by coupling the two instruments. Genesis SW collector surface contamination is the major issue hindering depth profile measurements of SW. The SIMS primary beam has the effect of mixing surface contaminants into the bulk during a depth profile, or gardening . Each profile is a superposition of intrinsic SW and contaminant signals. Back-side depth profiling of Genesis Si wafers has removed this concern, however it remains a tedious and time-consuming process involving manual thinning of the Si wafers. We also propose to gently sputter clean large areas of the top sides of the Si wafers using low-energy and massive molecular ion beams in the SIMS. For SW Fe and Ni measurements, we propose to use an F- primary ion beam, which has been shown to increase the useful yield of metals such as Ni and Cu from a Si substrate by two orders of magnitude relative to yields from conventional O primary beams. Image depth profiles will also allow us to post-process

the data and remove any remaining contaminant spots. We propose to request cleaned samples of both Si and sapphire (Al2O3) collectors from the bulk SW regime from the curators at Johnson Space Center. Using negative primary ions, e.g., O-, O2-, F-, SF5-, we can avoid charging issues on the insulating sapphire samples that would otherwise be present with O2+ primary ions, which are currently used to measure positive secondary ions in Si.

Gary Huss/University of Hawaii, Honolulu
Analyzing Genesis solar wind samples by ion microprobe.

The Genesis Mission was carried out to return a sample of the solar wind to Earth in order to obtain precise isotopic compositions and abundances of the elements in the solar wind. Our laboratory has been analyzing Genesis samples for several years and we have developed state-of-the-art techniques to obtain high-precision isotopic and elemental compositions. We collect back-side depth profiles in image mode, using raster ion imaging to collected image stacks that we can then process. Each pixel in the image is a depth profile. We align the stack in X and Y to account for beam drift. Then we align the pixels in the image so that the peak of the solar wind and the breakthrough at the surface are at the same depth in all pixels. We then combine the pixels to produce the final depth profile for that measurement. We have also learned how to reliably standardize the measurements. We propose to leverage what we have learned to make measurements of the fluences and isotopic compositions of a variety of elements in the Genesis collectors. Using a Cs primary beam, we will measure C, O, and S in Si collectors and Si in sapphire collectors. Using an O primary ion beam, we will measure Al, Ca, Cr, and Fe in Si collectors and Na in either DOS or sapphire collectors. Techniques will have to be developed to work the the sapphire collectors, but our preliminary work shows how this can be done.

The team consists of Gary Huss and Elizabeth Koeman-Shields of the University of Hawai I (UH), Andrew Westphal, Anna Butterworth, and Christine Jilly-Rehak of UC Berkley, Ryan Ogliore of Washington University at St. Louis (Wash. U), Munir Humayun of Florida State University (FSU), Don Burnett of Caltech, and Amy Jurewicz of Arizona State University (ASU). Sample preparation will be done at Berkeley, standardization will be done collaboratively between Berkeley, UH, FSU, ASU, and Caltech, the measurements will be done at UH, pit depths will be measured at ASU, and the data reduction will be done at UH with input from Berkeley and Wash. U. Papers reporting the data will be written at UH, although the entire team will have input into the final document.

This work will help maximize the scientific return of the Genesis mission though direct analysis of samples that Genesis returned to Earth. The Genesis mission is explicitly called out in the request for proposals as one of the targets for the LARS program (C.18 2.1.1).

Accompanying this proposal is a Planetary Major Equipment request to obtain a new RF Plasma Oxygen Ion Source for the Cameca ims 1280 ion microprobe. This source would

greatly facilitate the work on elements that make positive ions (Na, Al, Ca, Cr, Ti, Fe, Mn, Ni, etc) by providing much greater long term stability (cleaning up our depth profiles) and a much smaller spot size (de-smearing our depth profiles). If we do not get the source, the work can and will still be done, but the uncertainties will be larger.

Alexander Meshik/Washington University
Analyses and Interpretations of Noble Gases delivered by Genesis and Stardust Missions - Phase 2

This is a continuation of our previous and ongoing efforts to accurately determine abundances and isotopic composition of noble gases in solar wind delivered by Genesis mission and spallogenic neon and helium in sub-micron cometary grains in the outermost layer of the aerogel collector flown on NASA's Stardust mission.

Over previous years we developed a customized 8-multiplier mass spectrometer (in collaboration with NU Instruments) and refined a laser technique for extraction of solar wind noble gases from cm-size Genesis collectors with depth profiling capabilities. The most abundant isotopes 36-38Ar, 82-86Kr and 129-136Xe are now measured with permil precision, but the precision of low-abundance 78-80Kr and 124-128Xe is not yet sufficient to solve isotope cosmo-chemistry problems. One of these problems is the origin of the enigmatic phase-Q, a minor fraction of primitive meteorites containing most of the planetary heavy noble gases. The isotopic composition of Xe in phase-Q can be approximated by linearly fractionated solar Xe with the addition of either Xe-HL (presumably from presolar nanodiamonds) or from 244Pu fission modified by isotope-specific chemical fractionation. In the latter case the origin of phase Q is seemingly local rather than presolar . With the present precision of 124-128Xe, both hypothesis have statistically indistinguishable likelihoods. But triple or even double the analytical precision for light solar wind Xe isotopes will allow us to determine which one of the two hypotheses is likely to be correct. We already have been allocated the solar wind collectors required to improve Xe counting statistics by factor of 2.

We made all necessary preparations to estimate Br abundance in the solar wind using the 79Br(n, gamma)80Kr reaction. According our examination of various neutron irradiated Genesis solar wind collectors, only pure uncoated sapphire (SAP) has an acceptable level of terrestrial Br contamination. We already have in our possession ~ 5 sq. cm of SAP, acquired reliable Br standards and discussed all details of time-split neutron irradiation with the Missouri Research Reactor, our neighbor and long-term collaborator. The multicollector mass-spectrometer Noblesse will be optimized for measurements of small excesses of Br-derived 80Kr on top of solar wind Kr in neutron-irradiated SAP.

The first in the US, our new Helix-MC+ mass-spectrometer is the only instrument in our lab capable of resolving doubly charged 40Ar++ from 20Ne+. After certain required modifications and assessing the reproducibility, pressure dependence and actual systematical and statistical errors, we will use our Helix-MC+ for independent verification of (1) light solar wind noble gases to resolve the existing controversy in SW-Ne composition measured in Zurich, Minnesota, and our lab; and (2) our earlier finding of spallation 21Ne in track-free aerogel flown on the Stardust mission. The latter will be complimented with the study of major target elements (Mg, Al, Si) in track-free aerogel at ALS facility at Lawrence Berkeley National Laboratory carried out by our

collaborators Ryan Ogliore and Andrew Westphall. The 21Ne irradiation record may lead to an estimation of the comet erosion rate before it is perturbed into the inner solar system.

We have 10+ years experience in analyzing solar wind noble gases delivered by Genesis, dedicated mass spectrometers, and customized laser extraction facilities to fulfill the goals of the proposed study which is in line with the goal of the LARS Program to maximize the science derived from planetary sample-return missions through the development of laboratory instrumentation and/or advanced techniques required for the analysis of returned samples and direct analysis of samples already returned to Earth .

Devin Schrader/Arizona State University

Constraining asteroidal formation and alteration conditions via microstructure and elemental compositions of sulfides from returned samples

To increase the scientific return of sample return missions, we aim to maximize the information gained from individual minerals. One mineral system that records a range of pre- and post-accretionary histories are the Fe-sulfides. They occur in a wide range of extraterrestrial materials and are attributed to forming through a range of processes in the early Solar System. Such processes include condensation, crystallization/exsolution, gas-solid/liquid reaction, thermal metamorphism, and aqueous-phase processing. Previous work on Hayabusa samples (asteroid 25143 Itokawa) implies their sulfides formed by thermal metamorphism (being LL5-6 material).

The compositions, morphologies, and crystal structures of sulfides are determined by their formation conditions including temperature, time, oxygen and sulfur fugacity, and aqueous and thermal history. We propose to investigate the structures, compositions, and context of sulfide minerals in samples returned by Hayabusa and compare these with sulfides in chondritic meteorites. We will constrain parent body formation conditions of asteroid Itokawa by studying analogous sulfides with petrographic context in chondritic meteorites. We will also develop a sulfide database to interpret conditions of formation for sulfides that will likely be found in samples returned by Hayabusa2 and OSIRIS-REx. We will identify candidate sulfide grains in chondritic meteorites via scanning electron microscopy (SEM) and electron probe microanalysis (EPMA), determine grain orientation via electron backscatter diffraction (EBSD), and extract representative samples via focused-ion-beam (FIB) techniques. We will study the composition, texture, and crystal structure of individual FIB sections of the sulfides via transmission-electron microscopy (TEM) to investigate correlations between formation mechanism, oxygen and sulfur fugacity, temperature, and cooling rate. We will conduct the same measurements on allocated sulfide-bearing Hayabusa samples.

We have identified sulfides (pyrrhotite [(Fe,Ni,Co,Cr)1-xS] and pentlandite [(Fe,Ni,Co,Cr)9-xS8]) in LL, CI, CM, and CR chondrites that record equilibration temperatures from 100 to 600°C. Studying sulfides in meteorites that retain their petrographic context allows comparisons between established geothermometers and thermodynamic variables. Since pyrrhotite-pentlandite intergrowths are uncommon in some meteorite groups, sulfides in small returned samples may only consist of pyrrhotite or pentlandite. Therefore, to understand sulfide formation in asteroids it is important to study sulfides in meteorites with well-known formation conditions to investigate

indicators of formation in both pyrrhotite and pentlandite. Petrographic, chemical, and thermodynamic analyses on sulfides in meteorites via SEM, EPMA, EBSD, and FIB-TEM will provide a diverse sample set of sulfides for compositional and microstructural investigations to compare with returned samples. The motivation for this research is to identify microstructural indicators of sulfide formation conditions so that pre- and/or post-accretionary formation conditions can be determined for samples that contain sulfides but lack petrographic context, as may be the case for returned samples.
This research is relevant to the scope of the Laboratory Analysis of Returned Samples (LARS) program, because it aims to &maximize the science derived from planetary sample-return missions . LARS is most appropriate for this research since it is relevant to the Scope of LARS in C.18: &direct analysis of samples already returned to Earth . The analyses of meteorites are appropriate because they will directly support the interpretation of returned samples (specified in 1.3.3, C.18). We will analyze Hayabusa samples already allocated and develop a timely database of chondritic sulfides to assist in the interpretation of sulfides in returned-samples of asteroid Ryugu by Hayabusa2 in 2020.

Rhonda Stroud/Naval Research Laboratory
Microanalyses of returned comet, asteroid and interstellar dust samples.

The goal of the proposed effort is to provide fundamental new information about the structure and composition of samples returned by the Stardust and Hayabusa missions. We will perform state-of-the-art scanning transmission electron microscopy (STEM) of: (1) Wild 2 cometary grains captured in aerogel and as impact residues in Al foil; (2) impact crater residues from the Stardust interstellar foils; and (3) individual Itokawa asteroid particles from the Hayabusa sample collection. To complement the STEM studies, we will continue and expand our correlated analysis approach. Our established protocol includes focused ion beam, ultramicrotomy, STEM, synchrotron-based X-ray absorption spectroscopy, and isotopic composition measurements. New technique developments will include the use of nano-infrared spectroscopy and X-ray computed microtomography. Isotope measurements will also benefit from the increase sensitivity provided by a new Hyperion oxygen source, to be installed on the NanoSIMS at the Carnegie Institution of Washington in early 2017. The STEM studies will take advantage of PRISM, the LARS-funded Nion UltraSTEM at the Naval Research Laboratory (NRL), which incorporates a cold field emission electron source that provides high energy resolution (0.3 eV), along with high probe current (> 100 pA) in sub-nanometer probe sizes, and high sensitivity electron energy loss and energy-dispersive X-ray spectrometers. Samples suitable for these studies have already been allocated to us by the NASA and JAXA curation teams, and are in our possession at NRL. Identification of new interstellar impact craters on foils mapped at NRL is ongoing, though collaboration with Andrew Westphal and the Foils@home effort. The expected science gains from the proposed research projects are: an increased understanding of the range of elemental and isotopic compositions, and structures of the most fine grained materials in comets; better knowledge of the range of particle size and composition of dust grains from the

contemporary interstellar dust stream; and detailed knowledge of the effects of space weathering on individual mineral grains from an asteroid regolith. This work directly targets the two primary goals of the LARS program, to maximize the science return from existing returned sample collections, including Stardust and Hayabusa missions, and to advance the technique development for improved analysis of existing and future returned samples.

Andrew Westphal/University of California, Berkeley
Identification and Analysis of Interstellar Dust in the Stardust Interstellar Dust Collector

The ISPE, a consortium organized to characterize the collection of materials on the Stardust Interstellar Collector, identified the impacts of seven particles that are consistent with an origin in the stream of interstellar dust from the local ISM. The ISPE consisted of six coordinated efforts: identification of impacts in the aerogel collectors through a distributed search called Stardust@home; extraction of candidate tracks; analyses of candidates using synchrotron-based x-ray and infrared microprobes; identification and analysis of impacts in the Al foils of the Stardust collector by SEM imaging and SEM/EDX; laboratory hypervelocity impact experiments of interstellar dust analogs into aerogel and foils; and numerical modeling of interstellar dust propagation in the heliosphere. Since the end of the ISPE, more Level 1 candidates have been identified and are currently under study. Also, in collaboration with Rhonda Stroud and Brad De Gregorio at NRL, we have recently launched a new aspect of the Stardust@home project, to enlist the help of volunteers in the effort to identify impacts in the Al foils. During the pilot phase of foils@home, <130 volunteers carried out <379,000 searches of <152,000 individual fields of view. 36 new candidates resulting from these searches are currently in progress.

The evidence for interstellar origin has been indirect. A measurement of the abundances of oxygen isotopes is critical for identifying particles of interstellar origin. A measurement that is significantly different from the solar system values is a smoking gun for interstellar origin. Such measurements are possible now in residues in impact craters. However, such measurements are not yet possible on the largest particles, which are captured in aerogel, because the sample preparation is not yet at a sufficiently mature stage.

Under previous support, we have been refining and extending current sample preparation techniques, based on the sample preparation protocols developed for the cometary Stardust samples, which are much larger than the interstellar dust samples. Here tracks in aerogel keystones are compressed, embedded in epoxy, and ultramicrotomed to produced ultramicrotomed thin sections and particles in potted butts. For the purpose of developing the protocols, Steve Jones at JPL produced aerogel tiles impregnated with Allende spinel separates,which have oxygen isotopic composition well down the CCAM line. While we showed that we could measure these particles successfully, our assessment is that this technique is
fundamentally too unreliable to be used for sample preparation for interstellar dust candidates.

Here we seek support to continue the Stardust@home project, to complete the search for impacts in the remaining interstellar collector aerogel tiles, and to continue the identification of impacts in the foils. We also propose to develop a completely new sample preparation technique based on Focused Ion-Beam (FIB) milling. All of the individual components have been demonstrated, but have not yet been integrated into a reliable sample preparation protocol. We will use high-angle ion milling in the FIB, similar to that used for ion-beam polishing for EBSD. During milling, we will use the capability of a new FIB currently being acquired by the National Center for Electron Microscopy at LBL to simultaneously monitoring the sample by SEM backscatter imaging and EDX. To mitigate the problem of sample charging, we will use Atomic Layer Deposition to deposit conductive layers inside the aerogel picokeystones. The resulting sample will be ideally suited for oxygen isotopic analysis using SIMS or nanoSIMS, and sufficient material should be available to allow for subsequent analyses. After verification through extensive testing, we will measure oxygen isotopic composition of existing and future interstellar dust candidates. The project is highly relevant to the LARS program.