Emerging Words 2015
Abstracts of selected proposals
(NNH15ZDA001N-EW)

Below are the abstracts of proposals selected for funding for the Emerging Worlds 2015 program. Principal Investigator (PI) name, institution, and proposal title are also included. 137 proposals were received in response to this opportunity. On February 22, 2016, 29 proposals were selected for funding.

Agee, Carl/University of New Mexico
Acquisition of a Scanning Electron Microscope

We request funding for the acquisition of a new scanning electron microscope (SEM) with attached energy dispersive X-ray spectrometer (EDS) system and integrated micro-X-Ray Fluorescence (XRF) source and color cathodoluminescence detector. Our present system, a JEOL model 5800 with low vacuum capability and an Oxford Isis 300 EDX analyzer, was installed in 1997. The microscope, although still in working condition, requires extensive upkeep and repair; many parts are no longer available and substitutes must be made, with repair parts often manufactured in house at the UNM machine shop. The Oxford EDX analyzer operates on a Windows 98 computer, and because of hardware limitations of the communication cards and software, cannot be upgraded to a more modern computer. A significant amount of our analytical work on planetary materials at UNM requires the use of X-ray maps over large areas (e.g. thin section scale) to conduct modal analysis or discovery of minor/trace phases. Because of the limitations imposed by our current outdated SEM, our ability to perform this crucial work is seriously limited.

The instrument proposed for this request is a TESCAN Vega3 and an IXRF EDS and micro-XRF source. The Vega3 provides a large stage and chamber with additional ports for future added capabilities. High sensitivity backscattered electron imaging and color cathodoluminescence options will be included with the TESCAN, along with a LaB6 gun for improved resolution. X-ray excited spectra (XRF) have a higher peak-to-background ratio and therefore an improved sensitivity for mid-range and heavy elements compared to EDS, whereas the EDS has good sensitivity for light elements (silicon and lower). The small spot size (10 micrometer spot) of the IXRF system is the smallest in the SEM-adapted XRF market, and approaches the size of the electron excited interaction volume for light elements. Thus, the two systems provide the light element analysis strengths of EDS and the heavy element sensitivity of XRF. The combination of analytical results of electron and X-ray excitation improves the overall accuracy of qualitative and quantitative analysis and enhances X-Ray mapping capabilities.

The rationale behind this acquisition is that we have a multi-faceted, active, productive, and dynamic NASA research program at the University of New Mexico that will be greatly enhanced by this acquisition. These researchers are associated with the Institute of Meteoritics and the Department of Earth and Planetary Sciences and are funded through numerous NASA research programs. Further, many members are active participants in selected and potential future Discover, New Frontiers, and Flagship missions and incorporating access to this instrument into their activities tied to these missions would be important for mission success. We have an extensive track record for SEM and EMPA use and management, and a long history for allowing access to our labs to the planetary science community.

Amari, Sachiko/Washington University

Investigating constituents of the solar system: Isotopes and organic matter in carbonaceous grains in meteorites

We propose to study carbonaceous grains extracted from the Murchison meteorite.
1) We will investigate nucleosynthesis and the original compositions of low-metallicity (~15% of solar metallicity) asymptotic giant branch (AGB) stars through studies of KFB1 and KFC1 grains. They are only presolar samples available to probe stars of metallicity of this low level.
We will obtain high-precision O and Si isotopic ratios to better understand the Galactic chemical evolution of these elements. We will analyze Al-Mg systematics, isotopic ratios of Ca, Ti and heavy elements, and theoretically examine the grain data.
2) We will examine nucleosynthesis in core-collapse supernovae through studies of KE5 and KFA1 grains. We will focus on isotopic analysis of heavy elements. Supernovae graphite grains have never been analyzed for isotopic ratios of heavy elements. High trace element concentrations will help us determine isotopic ratios to probe nucleosynthesis in core-collapse SNe and distinguish types of core collapse supernovae (SNe). We will also examine Al-Mg and Ca-K systematics, analyze Ca and Ti isotopic ratios, and theoretically investigate the grain data.
3) We will investigate organic molecules formed in low-metallicity AGB stars and supernovae in presolar graphite grains, and those formed in interstellar medium and/or in the solar system in normal KFA1 grains using microprobe two-step lase mass spectrometry. We will obtain molecule specific 12C/13C ratios of the organic molecules, compare with those of host graphite grains. If they agree each other, it proves that the organic molecules formed in the stellar environment. Examination of KFB1 and KFC1 grains is the only way to learn how organic molecules form and evolve in C-rich AGB stars. If we detect indigenous organic molecules in SN grains, this will be the first identification that organic matter produced in SN ejecta.
4) We will analyze D/H ratios of normal KFA1 grains to probe the origin of these grains: whether they formed in the interstellar medium or in the solar system.

The strategic science question of the Emerging Worlds program is How did the Sun s family of planets, satellites, and minor bodies form and evolve? The investigations summarized above will clearly provide better answers to this question.

Barr Mlinar, Amy/Planetary Science Institute
Formation and Early Evolution of Earth's Moon

New measurements of stable isotope ratios, crustal thickness, and exposures of olivine on the lunar surface call into question existing ideas about the origin of the Moon via giant impact, lunar accretion, and structure of the primary lunar crust.

We will address:
Task 1: Can the giant impact create a Moon with the proper mass, angular momentum, iron fraction, and stable isotope ratios?
Task 2: Can the Moon accrete from an impact-generated disk with a magma ocean depth consistent with the lunar crustal thickness?
Task 3: What is the source region for olivine on the lunar surface, and what does this tell us about the vertical structure of its crust?

To answer these questions, we will:
1. Perform the first shock code simulations of the Moon-forming impact with realistic strength models in addition to realistic equations of state
2. Create a new model of the thermal evolution of a growing solid planet
3. Perform the first calculations of global impact-induced excavation on the Moon.

The goal of Tasks 1 and 2 is to understand how the Moon formed, which is relevant to the Emerging Worlds goal of understanding the formation, accretion, and stability of Solar System bodies.

The goal of Task 3 is to understand how impacts excavate material onto the lunar surface, and is relevant to the Emerging Worlds goals of understanding processes that occur on Solar-System bodies during the period of global differentiation, and planetary-scale events that affect global differentiation.

Borg, Lars/Lawrence Livermore National Laboratory
Isotopic Studies of the Early Solar Nebula and Primordial Planetary Differentiation

Goals: This work seeks to constrain the origin of material present in the proto-planetary disk near the time the first solids condensed, and to determine the timescales of planetary differentiation of terrestrial bodies, such as the Moon and Mars.
Methods: Task 1: Nd isotopic investigation of chondritic meteorites. High precision Nd isotopic measurements will be completed on primitive meteorites in order to determine if variations in 142Nd/144Nd observed in these materials results from nucleosynthetic processes. A nucleosynthetic cause for isotopic variation will be manifest by abundance correlations between 142Nd and the r-process isotopes 148Nd and 150Nd.
Task 2: Sn-Te isotopic systematics of CAIs. Stable Te isotopic measurements will be completed on CAIs in order to seek evidence for live 126Te. 126Te is produced by the decay of 126Sn (t1/2 = 260 ka), which in turn is produced only in a supernova. Evidence for live 126Sn would therefore require injection of supernova material into the proto-planetary disk just prior to CAI formation.
Task 3: Determine the heavy stable isotopic composition of CAIs. We have demonstrated previously that individual CAIs from the Allende meteorite have both excesses and deficits of r-process nuclides that depend on the atomic number of the element suggesting that material from a supernova was added to the nebula after CAI formation ceased. We seek evidence in support of this hypothesis in the isotopic composition of other heavy stable isotopes Er, Yb, and Hf, present in CAIs, based on the prediction they will demonstrate measurable, but progressively smaller, deficits in r-process isotopes.
Task 4: Chronologic investigations of CAIs. Sm-Nd and Lu-Hf, and Rb-Sr isotopic investigations of CAIs from several carbonaceous chondrites will be undertaken in order to evaluate initial isotopic compositions of materials present in the early Solar nebula. We have completed Sm-Nd chronometry of Allende CAI Al3S4 and demonstrated that the isotopic systematics of at least some CAIs are undisturbed.
Task 5-6: Chronologic investigations of lunar ferroan anorthosite suite rocks. Although these samples are thought to represent the oldest lunar crustal rocks, we have obtained a reliable young of 4.36 Ma on FAN 60025. This age is concordant with model ages for mare basalt formation, urKREEP solidification, and the peak of zircon ages. However, it is younger than several Pb-Pb zircon spot ages implying the FANs are either not primordial solidification products of the Moon, or the Moon differentiated relatively late in Solar System history. We will evaluate these possibilities by completing additional age determinations on several FAN suite rocks.
Task 7: 142Nd isotopic investigation of ancient martian basalts. Bulk rock 142Nd/144Nd-143Nd/144Nd compositions of shergottite meteorites suggest their source regions formed at 4504 Ma. Although this type of age is interpreted to represent planetary differentiation, the limited range of crystallization ages of these samples implies they are derived from a few relatively small regional-scale reservoirs. In order to evaluate whether the whole rock model age represents a global differentiation event, Nd isotopic compositions and precise ages of older martian meteorites, such as NWA8159 and NWA7635, will be determined.
Relevance: The work proposed here is relevant to the Emerging Worlds Program because it is focused on the chemistry of events and materials that contributed to the formation of planets, satellites, and minor bodies. Furthermore, the tasks designated here will constrain nebular, as well as planetary scale chemical and isotopic fractionation processes that occurred early in Solar System history. In particular, this proposal addresses processes associated with global differentiation that result in the separation of bodies into compositionally distinct layers.

Brandon, Alan/University of Houston

The Search for Nebular Heterogeneity and the Compositions of Terrestrial Planetary Materials Using Nd, Sm, and Os Isotopes

Understanding mixing in the solar nebula, the nature of solar and presolar components present, and origin of terrestrial bodies including accretion and early differentiation, is fundamental to constraining the origin of our Solar System and its early evolution. To examine these issues high-precision Nd, Sm, and Os isotope measurements will be performed on a wide range of bulk chondrites. New refinements for measuring Nd using the multistatic technique, results in improved external precisions of ±3 to 5 ppm (2 sigma) for 142Nd/144Nd. Measurements to date on chondrites largely used the static technique which has been shown to produce analytical artifacts such that internal precisions on 142Nd/144Nd of up to ±5 to 8 ppm cannot be reproduced to better than ±15 ppm from external reproducibility. Because the range of 142Nd/144Nd for all chondrites is ~50 ppm with large overlaps between different chondrite groups, determining the types of materials that make up terrestrial planets, or resolving distinct differences in their nucleosynthetic components on the bulk sample scale cannot be achieved with the present dataset. We will measure bulk chondrites spanning a wide range of metamorphic conditions, to determine whether the variability in Nd isotope abundances reflect acid resistant presolar grains with large s- or r-process isotope anomalies that were not accessed in the digestions. In addition, we will use the established alkali fusion technique on a subset of the samples to independently examine whether acid resistant pre-solar grains are accessed in bulk sample digestions. Further, correlations between s-process 142Nd with r-process dominated 145Nd and 148Nd are hinted at within the present database but with unconvincing, large scatter. The new, higher-precision data proposed in this study will examine how much of this may reflect unmixing of s- and r-process Nd in bulk chondrites. Complementary Sm isotope data will be obtained on the same bulk chondrite fractions to investigate the previously observed effect on 144Sm of p-process deficiencies and how these impact production of 142Nd from p-process 146Sm and potentially leverage observed variation on 142Nd/144Nd. High-precision Os isotope measurements will be performed on bulk fractions of CV-CK and ordinary chondrites spanning a wide range of metamorphic conditions. With these new bulk rock data we will examine the issue of nucleosynthetic component distribution and variability on the scale of chondrite parent bodies. Leaching/residue-combustion experiments will also be performed on unequilibrated ordinary chondrites. These complement studies on leaching/residue-combustion of carbonaceous and enstatite chondrites elsewhere and examines whether the s- and r-process components for Os are from the same stellar environments between the chondrite groups or whether multiple nucleosynthetic components were dispersed in the nebula heterogeneously. Neodymiun, Sm, and Os are all refractory elements and hence provide complementary constraints on the distribution of nucleosynthetic isotope anomalies in these materials. This issue can only be examined by obtaining high-precision isotope data from these early-formed Solar System samples. Hence this will lead to a better understanding of the earliest history of the Solar System from the seeding of nucleosynthetic components, nebular condensation, accretion into terrestrial bodies and their early differentiation. This research is consistent with the Scope of the Emerging Worlds program. Our new data will provide fresh insights into how the Solar System formed and evolved from protoplanetary disk formation and evolution, chemical and physical processing of nebular dust, bulk properties of Solar System bodies, formation, accretion, early thermal and chemical processing, and global differentiation of Solar System bodies. Such data will also help in planning for missions that will target specific bodies in our Solar System.

Charnley, Steven/NASA Goddard Space Flight Center,
Organic Chemistry in the Earliest Phases of Solar System Formation

The principal goals of this project are to construct chemical models of the organic and isotopic chemistry which occurred during the early evolution of the Solar Nebula. The fundamental importance of this study for Emerging Worlds lies in the fact that all the starting materials available for the assembly of planetary systems must be obtained from the reservoir of the interstellar medium (ISM). For comets, the important issue is elucidating how much of their organic composition and chemical heterogeneity can be attributed to being pristine ISM, or partially processed ISM, or purely nebular, or a complex mix of the three. For meteorites, an additional major question is the extent to which the large isotopic enrichments seen in interstellar molecules first survived incorporation into the nebula.

Theoretical models of the volatile chemistry can be constrained both by astronomical observations and by comparison with the measured composition of primitive Solar System material. Recent observations by ground-based interferometers at mm/submm wavelengths by interferometers such as the {\it Atacama Large Millimeter/Submillimeter Array} (ALMA), are beginning to reveal the fine chemical details of the disk accretion shock. However, until now there have been very few detailed studies of how the accretion process affects the volatile organic material, and none addressing possible isotopic effects. We will model the processing of organic interstellar matter as it collapses and passes through the nebular accretion shock and becomes incorporated in the nebula. We also propose to perform detailed theoretical studies of the molecular chemistry which occurred when accretion onto the nebula disk was episodic and infalling material in the protosolar envelope experienced a series of transient heating events, as in FUor outbursts. We will determine the importance of these nebular accretion scenarios for the organic and isotopic chemistries, to quantify differences with pristine interstellar material and for comparison with the characteristics of primitive organic matter.

Relevance to NASA Emerging Worlds Program: Our proposed research falls at the interface between the formation of the nebular disk and the beginnings of nebular chemical evolution. It is is highly relevant to the Emerging Worlds Program. as it considers chemical studies of the earliest phases of protoplanetary disk formation. Issues to be addressed include chemical processing gas and ices, isotopic fractionation, the formation of complex molecules, and their relation to the chemical properties of ancient materials.

Cody, George/Carnegie Institution of Washington
Investigating D, 13-C and 15-N Exchange Mechanisms and Kinetics in Insoluble Organic Matter associated with Chondritic Parent Bodies

Investigating D, 13-C and 15-N Exchange Mechanism and Kinetics in Insoluble Organic Matter associated with Chondritic Parent Bodies

Scientific Goals and Objectives: Chondritic meteorites record unique information about early Solar System processes. Up to several wt. % of chondritic meteorites exists in the matrix as organic solids (Insoluble Organic Matter, IOM), a highly complex macromolecule in terms of chemistry (i.e., organic functional group composition), isotopic composition (D, 13-C, and 15-N), and physical morphology. Significant and systematic variation in molecular structure of IOM has been shown to be the result of processing (aqueous, oxidative, and/or thermal) within the interiors of planetesimals. Recent evidence has shown that some D-H exchange occurs between IOM and water (now bound in clays), but the D remains more enriched in IOM than residual water. A systematic study of the recently available Tagish Lake clasts reveals a progression in D-H exchange between IOM and water with extent of alteration, although the extent of exchange even in the most altered IOM remains incomplete. If the thermokinetics of D-H exchange between IOM water were known, this information could be used to provide a powerful constraint on temperature and time of aqueous processing. Small variations in IOM s 13C and some very large variations in IOM s 15N abundance may also be due to exchange. In recent work simulating the formation of IOM experimentally, it is observed that incorporation of nitrogen (as NH3aq) is facile and likely reversible. Thus, 15N isotope exchange might reasonably be expected under aqueous processing. There is one plausible route that is worth exploring that enables carbon isotope exchange between carboxyl groups and carbonate ions. Linking the experimentally derived thermokinetics of each of these processes will place considerable constraint on time-temperature parameterization in planetesimal interiors.

Methodology: The proposed research will rely heavily on laboratory synthesized IOM that has been shown to be nearly identical to actual chondritic IOM in terms of chemistry (functional group concentrations) and physical morphology. We are testing the hyptothesis that IOM formed post accretion in planetesimal interiors. Hydrogen, carbon, and nitrogen isotope exchange experiments will be performed as a function of time over a series of temperatures to obtain the relevant thermokinetic parameters. Exchange will be measured using both Solid State Nuclear Magnetic Resonance (NMR) Spectroscopy (1H, 2H, 13C, and 15N are NMR active nuclei) and Fourier Transform Infrared (FTIR) Spectroscopy (for D-H exchange). Isotope exchange under dilute condition will be determined using Isotope Ratio Mass Spectrometry (IRMS). The effect of temperature and temperature history on IOM molecular structure will be determined using 13C SSNMR as will the post synthesis alteration during extended aquathermolytic processing. After characterizing the synthetic IOM and determining the relevant thermokinetic exchange parameters, we use these to model plausible thermal histories in planetesimal interiors.

Relevance: This research is directly relevant to the Emerging Worlds Program s focus on understanding the formation and early evolution of our Solar System . Our results will have implications for: (i) the formation of organics and ice, and their transport in the disk, (ii) the accretion locations, thermal histories and dynamical evolution of asteroids, and (iii) the delivery of volatiles and organics to the terrestrial planets.

Ebel, Denton/American Museum of Natural History
Chemistry and Architecture of Meteorites: Constraints on Astrophysical Models and Ground Truth for Exploration

We seek to understand the formation and early evolution of the Solar System and to simultaneously gain insights into asteroids, which are both mission targets and threats to our planet. We propose an interdisciplinary plan to investigate the physics and chemistry of large and small scale processes forming solids and liquids in the gas phase of the protoplanetary disk, and to understand how those materials accrete into larger bodies. Studies include a combination of astrophysical-cosmochemical theory and modeling; textural, petrological, and chemical studies of meteorites; and laboratory experiments to test chemical model predictions.

Petrological work will include surface chemical and volumetric 3-dimensional CT mapping of meteorites to allow tests of astrophysical theories of how chondrules and matrix accreted into larger bodies, and how chondrules might be size-sorted. The 3D CT will also allow density estimates of chondrule populations. This is complemented by position-sensitive x-ray diffraction for modal mineral abundances (at CUNY). We will focus on selected ordinary chondrites (the most abundant primitive meteorites) and CR chondrites, to measure the abundance and sizes of their millimeter-sized chondrules, and the distribution of elements among chondrules and matrix. We will also apply the same tools to the very different CM chondrites. The 3D CT will involve student investigators at Fordham. This work will increase our understanding of asteroid physical properties and clarify how we could use chondritic bodies as in situ resources for space exploration.

Chondritic asteroids grew from small solids in a gas-rich disk around the early sun. We will apply theory and modeling to investigate how gas and solid chemistry varied in time and space around the sun, and how chemistry affected and was affected by physical phenomena such as magnetic fields and dust opacity. To do this, we will integrate our chemical models with astrophysical dynamical codes to simultaneously address disk chemistry and physics. This work will be informed by our petrological studies, which provide tests of hypotheses developed using models.

In the laboratory, we will continue tests of selected predictions made by our chemical models that describe partial or complete equilibrium among silicate solids and liquids condensing from hydrogen-rich disk vapors. Real outcomes of this process are recorded in the chondrules and other inclusions in meteorites. These tests provide "ground truth" for models, and provide new calibration points for future, improved chemical models.

Trace elements such as the rare earth elements can provide evidence of conditions in the early solar system, because their partitioning is controlled by temperature and oxygen abundance. We will investigate trace element partitioning among minerals, silicate liquids, and vapor both in the lab and by application of theory. We will measure these distributions among chondrite components. We will use those results to interpret the distributions of trace elements among components in a range of chondrite types, to test astrophysical-cosmochemical hypotheses for the origins of components and their accretion.

Upon completion of discovery and interpretation, we will disseminate our results to the scientific community through peer-reviewed publications, and to the public through presentations and museum-based informal education. All of this work will address the Emerging Worlds goal of understanding "how the Sun s family of planets, satellites, and minor bodies (including small bodies and rings) form and evolve", and matches NASA's particular interest in "research projects that closely support its mission for exploring the Solar System, contribute to the development of future missions, or involve major interdisciplinary efforts to solve key questions" (ROSES 2015 C.1-10).

Floss, Christine/Washington University
Constraining the Origin(s) of Meteoritic Nanodiamonds Through Correlated Transmission Electron Microscopy and Atom Probe Tomography Analyses

Meteoritic nanodiamonds have been extensively studied since their initial identification and association with highly anomalous Xe isotopic ratios, but their origins remain poorly understood. Isotopic anomalies present in several trace elements indicate a stellar origin, but near-solar C and N isotopic compositions suggest formation in the solar system. In order to constrain the origins of nanodiamonds and to determine whether distinct populations are present in the residues, measurements of individual meteoritic nanodiamonds are needed. Atom probe tomography (APT) is currently the only technique that has the spatial resolution and sensitivity needed to measure these tiny ~3 nm grains. In our past work we have developed sample preparation techniques and instrumental protocols for analyzing diamonds as nanometer-scale inclusions in a host matrix, and have demonstrated the feasibility of measuring individual or small clusters of nanodiamonds using this approach. Here we propose continued APT analyses of meteoritic and synthetic nanodiamonds in order to determine minor element abundances and quantitative C isotopic ratios of individual nanodiamonds. This will allow us to evaluate what fraction (if any) of nanodiamonds is presolar and whether there are different populations with distinct isotopic and/or minor element properties.

We will combine our APT work with correlated transmission electron microscopy (TEM) of the microtips used in the atom probe. This will allow us to correct for the local magnification effect observed in APT and obtain more accurate reconstructions of our microtips. In addition, we will compare the crystal structure of the C residue with the reconstructed mass-to-charge-state ratios obtained by APT, which will let us distinguish between the nanodiamonds and amorphous C phases that are also known to be present in the residues.

The proposal team will consist of PI Christine Floss and Co-I Tyrone Daulton, at Washington University in St. Louis, and Co-Is David Seidman and Dieter Isheim who run the Cameca Local Electrode Atom Probe at Northwestern University. In addition, we will request funding for a graduate student to carry out much of the work.

Our research supports the goals of NASA s Emerging Worlds Program to explore and observe the objects in the Solar System to understand how they formed and evolve , as outlined in the ROSES 2015 NRA and is, therefore, relevant to NASA s strategic objective to ascertain the content, origin, and evolution of the solar system& .

Grove, Timothy/Massachusetts Institute of Technology
Experimental and Petrologic Investigations of Chemical Differentiation on the Ureilite Parent Body

The objective of this research program is to understand the early evolution of the ureilite parent body (UPB). Ureilite meteorites are some of the most ancient achondrites and they record metal - mineral - melt processes (smelting) that occurred within one to two million years after the condensation of solids from the solar nebula. Understanding the processes of ureilite formation is very important for understanding the very earliest planetary differentiation processes in the solar system. Though they are considered to be enigmatic the chemical and the mineralogical variability within the group preserve these processes. We propose phase equilibrium studies to determine the physical conditions and chemical consequences of melting processes that occurred in the ureilite parent body in the presence of metal and carbon. Appropriate natural and/or synthetic carbonaceous chondrite starting materials will be used to determine partial melting and crystallization behavior over the pressure range of 1 to 50 MPa; conditions relevant to differentiation within the parent body. The ureilite experiments will be carried out using a gas medium apparatus (in MHC - Molybdenum-Hafnium Carbide ultra-high temperature gas pressure vessels) in the presence of graphite and CO gas. These experiments will provide new constraints on the conditions and processes that lead to the compositional and mineralogical variations observed in ureilite meteorites. Ureilites are residues from a smelting process whereby FeO in the silicates reacts with graphite to form Fe metal, magneisan silicate and CO gas. For the first time, the experiments will provide the compositions of the melt that was in equilibrium with the complementary smelted ureilite residue. These melts have never been identified in our meteorite sample, and perhaps we will identify them among the existing sample set or in future new finds. We will obtain compositional information on the low degree melts that form at the beginning of smelting, and track the change in melt and residue composition over the appropriate range of smelting. The experiments will also determine the pressure and temperature dependent changes in the proportions of silicate metal carbon melt involved in the smelting process. These phase proportions are critical for quantitatively understanding the amounts of metal and carbon that are involved in the smelting process and in tracking the compositional evolution of the UPB and the likely structure of the parent body during smelting. The higher-pressure melting experiments will provide a calibration of the depth silicate Mg# correlation in ureilite residues. To complement these studies we will perform petrologic and large-scale x-ray mapping using the electron microprobe to determine the proportions of silicate, metal and graphite in a suite of carefully selected ureilite meteorites.

The proposed work will provide new experimental and petrologic constraints that will be used to test models of chemical differentiation in small meteorite parent bodies, and is specifically aimed at the ureilite parent body. Our proposed laboratory experiments and petrologic studies of ureilite meteorites are relevant to three elements of the Emerging Worlds Program. The work will provide fundamental constraints on: 1) the formation, accretion and stability of early Solar System bodies, 2) the chemical and physical properties of ancient materials (asteroids) and 3) the origins of meteorites and meteorite groups.

Harker, David/University of California, San Diego
Emerging Comets from Protoplanetary Processes

Relevance: Solar system formation is an engine that simultaneously preserves and transforms interstellar medium (ISM) dust grains into planetesimals and, ultimately, planets. Being a mixture of ISM dust and solar nebula processed material, comets allow us to investigate both the inputs and outputs of dust transformation in the young Solar System. Dust grains in the ISM are dominated by amorphous silicates, i.e., they have chemical composition (stoichiometry) similar to pyroxene and olivine. Studies of silicates in the galaxy constrain f_cryst < 5% by mass In contrast, dust ejected by comets, such as C/1995 O1 (Hale-Bopp) and 9P/Tempel 1, have significant crystalline mass fractions: 60 80% of Hale-Bopp and ~30% of 9P. Taken together, the observations of the ISM and of comets strongly suggest that amorphous ISM dust was either destroyed and re-condensed as crystals, or that it was annealed (crystallized), prior to the accretion of planetesimals in the icy outer-disk. Determining the dust composition of comet nuclei helps us understand (A) how dust formed in the inner-Solar System, and (B) how that dust was transported to the outer-Solar System; processes that are apparently ubiquitous in observations of external protoplanetary disks.
The composition, size, and porosity of cometary dust provides a view into the earliest planetforming processes that occurred in the Solar System. Grains formed, were radially mixed, and agglomerated before being preserved in comet nuclei. Thus, comets hold a record of those processes that occurred in the disk before they formed. In addition, measuring the dust properties of many comets will develop into a dust-based comet taxonomy with which we may test formation scenarios of the two comet dynamical families Jupiter-family comets, and Oort cloud comets.
Methodology: We propose to analyze spectra from the Spitzer Space Telescope Archive. Spectra from the IRS instrument covers the critical 8 to 12 micron silicate emission features, but also has the broad wavelength coverage (5 to 35 micron) necessary to constrain grain size distributions. We identify the features of amorphous and crystalline silicates directly from 8 13 micron spectra. Thermal emission models of the coma will be fit using chi-squared minimization to observed mid-IR spectra to constrain the grain size distribution, porosity, and the relative mineral abundances, which include amorphous carbon, and amorphous and crystalline silicates A spectral resolution of R > 100 and a signal-to noise ratio of > 10 is sufficient to constrain the amount of silicate crystals a primary goal of our project.
Science Goals: 1) Ascertain the range of comet dust properties extant in the early solar system through comet comae; 2) Constrain the amount of high temperature condensates (i.e., crystalline silicates) present in the outer solar system; 3) Test our dataset for nucleus heterogeneities and posit whether or not it may arise from mixing in the disk after planetesimals formed.

Ishii, Hope/University of Hawaii, Honolulu

Insights into Origins and Inter-relationships of Amorphous Silicates from Primitive Solar System Bodies

Amorphous silicates are arguably the least-understood solids in extraterrestrial materials, despite comprising the majority of rock-forming material in the interstellar medium (ISM) from which our Solar System evolved. Their significance arises from astronomical observations that ISM silicates are >99% amorphous, while protoplanetary disks contain a fraction of crystalline silicates varying by heliocentric distance (and from disk to disk). Thus, amorphous (a-) silicates in comets and primitive meteorites are potential survivors from the original interstellar a-silicate population that dominated the presolar dust from which the Sun and Solar System formed. It remains an open question how much of the ISM presolar a-silicates survive in recognizable form in primitive bodies. Since a-silicates are, by nature, metastable, they are more susceptible than crystalline solids to alteration prior to, during and after release from their parent bodies. Despite their vulnerability, at least some a-silicates retain unambiguous evidence of a pre-solar origin demonstrated by non-solar isotopic compositions.

The goal of this interdisciplinary proposal is to improve understanding of the inter-relationships - or lack thereof - between a-silicates in comets and asteroids, those small primitive solar system bodies subjected to the least alteration since accretion, and their relationships to ISM a-silicate grains characterized by astronomical observations and modeling. Samples include a-silicates from A) chondritic porous interplanetary dust particles (CP IDPs) consistent with cometary origins, B) fine-grained matrices of highly pristine (minimally-altered) chondrites, and C) samples returned from comet 81P/Wild 2. Existing data are incomplete and, in general, cannot be compared side-by-side due to measurement differences. We propose three primary research tasks: 1) We will perform a thorough, side-by-side (scanning) transmission electron microscopy ((S)TEM) comparison of a-silicates in CP IDPs and ultracarbonaceous micrometeorites, pristine chondrite matrices and 81P/Wild 2 dust to study bonding, chemistry, textures, petrography and water content. We will identify the least-altered cometary and meteoritic samples and compare their a-silicates to ISM a-silicate characteristics established from observations, and we will report on those physical characteristics of a-silicates identified by our astronomer collaborators as critical to improving astrophysical modeling and fitting of cometary and ISM silicate spectra. 2) We will carry out in situ (S)TEM heating and annealing of a-silicates in CP IDPs, chondrite matrices and comet 81P/Wild 2 samples in vacuum. This will establish the upper limits of temperature experienced by these objects during their formation, incorporation on their parent bodies, release, interplanetary travels and eventual collection. The results may provide a means of distinguishing between different formation mechanisms as well as potential different populations that experienced different processing among texturally and compositionally similar a-silicates. 3) We will subject a subset of minimally-altered a-silicates in each sample set to ex situ hydration experiments at fixed temperatures followed by (S)TEM analysis to determine how a-silicates in each sample type evolve with aqueous processing. From these data, we will explore the likelihood of processing relationships between cometary a-silicates and asteroidal matrix components. This work will ultimately help establish how widespread surviving interstellar a-silicates may be in small solar system bodies.

The proposed work is relevant to NASA's strategic science question, "How did the Sun's family of planets, satellites, and minor bodies form and evolve?" and the Emerging Worlds Program goal to understand the formation and early evolution of our Solar System via the focus on understanding the a-silicates found in primitive materials from comets and asteroids.

Jackson, Alan/Arizona State University
Stop hitting yourself: did most terrestrial impactors originate from terrestrial planets?

We propose to study the influence of debris released by giant impacts on the late formation and evolution of the inner solar system, using dynamical methods and results of impact simulations.

Although the asteroid belt is the main source of impactors in the inner solar system today, it contains only 0.05 Lunar masses of material. While the asteroid belt would have been much more massive when it formed, it is unlikely to have had greater than a Lunar mass since the formation of Jupiter and the dissipation of the solar nebula. By comparison, giant impacts onto the terrestrial planets during the late stage of accretion typically released debris equal to several per cent of the planet's mass into heliocentric orbit. The Moon-forming impact on Earth, for example, released over a Lunar mass of debris, more than has ever been contained in the asteroid belt. The Borealis basin impact on Mars released more debris at once, than the present day asteroid belt.

Escaping impact debris is less long lived than the main asteroid belt, as it is injected on unstable, planet-crossing orbits. This same factor however also increases the impact probability with the terrestrial planets and asteroids. With such a large amount of mass it seems highly likely that these now-extinct populations of impactors should have played an important role in the evolution of the solar system, much as now-extinct radionuclides played an important role in the thermal histories of solar system bodies.

One of the most obvious effects of re-impacting debris is the production of craters. The Moon, Mars, Mercury and the largest asteroids may be expected to display evidence of re-impacting bombardments in their crater record, subject to their thermal state and subsequent surface re-processing. However, in understanding the cratering history of the Solar System, the contribution of giant impact debris has been almost universally neglected, and constraining this contribution constitutes our primary task.

In addition to the production of surface craters, large impacts can punch through the lithosphere and exhume material from large depths. This is particularly pertinent for re-impacts onto a progenitor body which will have a deep magma ocean after the giant impact. Depending on the size and composition of the target, this magma ocean may form a flotation crust as on the Moon and perhaps Mercury, that would act as an insulating blanket. Impactors that punch through or disrupt this crust may allow the magma ocean to cool faster. Conversely, for magma oceans that freeze from the bottom up, the energy input from re-impacts may keep them liquid for longer. This feeds back into the cratering record as craters will only be recorded once there is a stable, solid surface. In this sense the dynamics of giant impact debris can in principle become a chronometer of planetary solidification. The influence of long term re-accumulation on planetary thermal evolution is our second task.

Our third task is to study re-impacting debris as an aspect of terrestrial satellite formation. The Moon, Phobos and Deimos likely formed from circumplanetary debris disks. These disks did not exist in isolation. They, and the satellites that form from them, would have been subject to re-impacts by returning debris from their formative giant impacts. Whether such disk impacts would have aided or hindered satellite formation is unclear.

Kaiser, Ralf/University of Hawaii at Manoa
Untangling the Formation of Alkylphosphonic Acids in Interstellar Analog Ices

Science Goals & Objectives: The overall goal of this project is to comprehend the formation of a key class of astrobiologically important molecules alkylphosphonic acids in interstellar ices as present in cold molecular clouds upon interaction with ionizing radiation. Cold molecular clouds are considered as nurseries of stars and planetary systems. The densest parts of these clouds eventually undergo gravitational collapse to form primitive material, which in turn supplies the basic ingredients for planets, their moons, and smaller bodies like asteroids and comets. Therefore, organic material such as alkylphosphonic acids, which initially formed in the molecular cloud, could have been incorporated into comets and parent bodies of meteorites such as of Murchison and might have been delivered to early Earth.
Significance: Our project has unprecedented implications on multiple levels: to rationalize a potentially exogenous source of organic, water-soluble phosphorus-bearing compounds that might have initialized the organic phosphorus chemistry on early Earth, to better understand the origin of alkylphosphonic acids as detected in the Murchison meteorite, and to interpret prospective data from the Rosetta mission on the molecular composition of comet 67P/ Churyumov-Gerasimenko.

Methodology: Our methodology is based on conducting laboratory simulation experiments, which mimic the interaction of ionizing radiation with low temperature, astrophysically relevant ices, and tracing the formation of alkylphosphonic acids on line and in situ in the solid state and upon warm-up of the irradiated ices in the gas phase. We exploit novel, emerging laboratory techniques, which have not been accessible in previous simulation studies. These techniques are: photolysis of ices with mono energetic photons, a concerted on line and in situ infrared, Raman, and ultraviolet-visual (UVVIS) spectroscopy of the photolyzed ices to detect functional groups of alkylphosphonic acids, and - upon their release into the gas phase - fragment-free photoionization of individual alkylphosphonic acids with tunable vacuum ultraviolet (VUV) photons coupled with reflectron time-of-flight mass spectroscopy (ReTOF-MS).
NASA Relevance: Results from this proposal directly overlap with the goals of NASA s Emerging Worlds Program: to conduct scientific investigations related to understanding the formation and early evolution of our Solar System and to answer the fundamental science question of how the Solar System formed and evolved. It covers the physics and chemistry of events and materials that are relevant to the formation of planets, satellites, and minor bodies. The Emerging Worlds program supports scientific investigations that contribute to the understanding of the chemical and physical processing of gas, dust, and ice. Our proposal tackles fundamental research with respect to the formation of alkylphosphonic acids in molecular clouds which eventually provide the basic ingredients for planets, their moons, and smaller bodies like asteroids and comets. Our proposal accounts for NASA s goal to investigate via laboratory studies the basic chemical processes that drive the chemical evolution of our Solar System. This project is very timely, since the Rosetta spacecraft arrived at comet 67P/ Churyumov Gerasimenko. Prospective publically disseminated data on the molecular inventory can be compared with the newly formed alkylphosphonic acids identified in our studies. Our project presents an exceptionally well-timed interdisciplinary opportunity to solve key question (origin of a key class of biorelevant molecules) and to support a concerted attack from both directions combining results from laboratory experiments and data from space missions ultimately revolutionizing our understanding of the formation of alkylphosphonic acids.

Kiefer, Walter/Lunar and Planetary Institute
Differentiation and Early Thermal Evolution of Meteorite Parent Bodies

There is abundant evidence that some meteorite parent bodies melted sufficiently to produce iron-rich cores. This includes the existence of 11 chemically distinct groups of iron meteorites, 182Hf-182W isotopic observations that require separation of lithophile Hf from siderophile W, and remnant paleomagnetism in 5 classes of meteorites (angrites, pallasites, eucrites, and CM and CV chondrites) that require the presence of a magnetic dynamo and hence a liquid metal core on the parent bodies of these meteorites. Moreover, several types of igneous meteorite, including eucrites, diogenites, angrites, aubrites, and urelites, require that silicate melting and crust formation occurred on at least 4 chemically and petrologically distinct meteorite parent bodies.

Most past studies of the differentiation of meteorite parent bodies assumed that metals and silicates melt at different temperature intervals, with metal melting in the range 940-960 °C and silicate melting beginning around 1150 °C. However, for geochemically realistic amounts of sulfur, melting in the Fe-FeS system is not complete until temperatures of 1350 to 1500 °C and thus strongly overlaps with silicate melting. In other words, if a meteorite parent body is undergoing silicate melting, then it must also be experiencing metal melting at the same time. For objects formed in the first 1.5 million years of the Solar System, radioactive heating by 26Al is extremely important and can result in melting of both metals and silicates. Core formation therefore involves a sort of iron rain , with liquid metal drops falling through a suspension of silicate crystals in a silicate magma.

The ability of an object to melt and differentiate depends on its thermal structure. Thermal evolution will be modeled using finite difference methods and will incorporate heat transport by thermal conduction, radioactive heating from short-lived (26Al, 60Fe) isotopes, the insulating effects of a low conductivity, porous surface layer that sinters to a high conductivity material above 700 K, and melting both of metal and of mantle silicates. The effect of convection (if it occurs) on heat transport will be modeled using a parameterized convection method. Differentiation of the crust and core will modify the subsequent thermal evolution by transporting 26Al to the crust and 60Fe to the core. A key feature of this study is that thermal evolution and differentiation models will be calculated for CM, CV, H, LL, and EH chondrite compositions using experimentally determined metal and silicate melting phase relationships that are appropriate for each composition. An important result will be a set of differentiation regime diagrams that quantify the fraction of metal melting, silicate melting, and the preservation of primordial crust as a function of object size and accretion time. Results will be tested using radiometric ages from systems such as 182Hf-182W and 26Al-26Mg that constrain the early evolution of the crust and core in these objects. Core formation by iron rain will be modeled using Stokes flow for a spectrum of initial metal drop sizes in order to assess the characteristic timescale for falling through the mantle to the core. The iron rain model has been studied for Earth and other terrestrial planets, but this will be its first application to a meteorite parent body. The partitioning of moderately siderophile elements between metal and silicates will be modeled as a test of the core formation model results. The core heat flux will be used to assess the core s ability to generate a magnetic dynamo early in Solar System history and thus to explain the remnant paleomagnetism in some meteorites. Finally, model results will also provide an improved calibration of the relationship between the core cooling rate and object size, and thus contribute to our ability to interpret metallographic cooling rates in iron meteorites.

Lissauer, Jack/NASA Ames Research Center
Formation of Jupiter, Saturn, Uranus & Neptune

Science Goals and Objectives:
We propose to attack, mainly through numerical modeling, some major outstanding problems in the core nucleated accretion theory of the formation of the giant planets in the Solar System. This work will account for important physical processes heretofore neglected and thereby provide a much more realistic model for the formation and early evolution of the giant planets. During the early stages of giant planet accretion, with a rocky core of around an Earth mass, the basal temperature of the hydrogen atmosphere above this growing core can already exceed a few thousand degrees, sufficient to allow evaporation of accreted planetesimals within the envelope. This may affect the growth of the giant planet, primarily by increasing the mean molecular weight of the envelope (reducing the pressure scale height), and it may also produce a wider range of possible outcomes for giant planet formation than those previously studied. The consequences may be partially preserved throughout subsequent evolution and influence the internal structure of the giant planets today. To study the effects of this process, we will compute the amount of mixing of the constituents within the planets during their growth. This additional physics will be incorporated into detailed numerical studies of the concurrent accretion of solids and gas, including an improved treatment of interactions of the growing planets with the surrounding protoplanetary disk.

The proposed work will address the following questions:
How much H and He was mixed with material from the heavy element "cores" of the planets during the formation epoch?
How much planetesimal material was dissolved into the H/He envelope?
How long did Jupiter, Saturn, Uranus, and Neptune take to form?
What was the solids surface density in the region of the protoplanetary disk where these planets accreted?
Do Jupiter and Saturn retain most of the angular momentum of the circumplanetary subdisks through which much of their mass was accreted, or did they shed most of this angular momentum?

Methodology:
Accretion of solids will be modeled using the PSI Multizone Code. The internal structure and evolution of each planet will be modeled with an adapted 1D stellar evolution code. Gas accretion will be followed with a 3D hydrodynamic code when appropriate.

Relevance to NASA's Emerging Worlds Program:
Our simulations will provide a substantially improved physical model of the formation of the four giant planets in our Solar System, particularly regarding the mixing of light and heavy components within the planet and in our treatment of the final stages of accretion when the planets' ultimate masses and heavy elements content were determined. We will determine whether or not a realistic amount of mixing of light gases with heavy constituents within Uranus and Neptune can yield planet structure models that match the planets' measured gravity fields without invoking super-solar ice/rock ratios. The interior structures of Jupiter and Saturn that we compute using mixing of constituents will be useful to interpreting the gravity data sent back by the Juno and Cassini Solstice missions.

Our proposal is for research that "aims to answer the fundamental science question of how (the largest planets within) the Solar System formed" and "thereby it provides context for the interpretation of ... Solar System observations that are relevant to its formation" (quotes from Appendix C.2 of ROSES-15).

McKeegan, Kevin/University of California, Los Angeles
A closure age for crystallization of the Lunar Magma Ocean: Re-examination by high precision zircon chronology

The timing of the solidification of the lunar crust is widely recognized as an important parameter in models of the giant impact origin of the Moon and, thus, of the formation of the Earth and the dynamical evolution of the inner solar system. However, various long- and short-lived chronometers yield data supporting different interpretations of the age of the Moon , with estimates varying from ~60 to more than 200 million years after the formation of calcium-aluminum-rich inclusions. We propose here to perform coupled U-Pb and Lu-Hf isotopic studies of individual selected lunar zircons to determine the timing of the primary silicate differentiation of the Moon, thereby providing a well-constrained date for the crystallization of the Lunar Magma Ocean and a firm lower bound on the age of the Moon. The focus of this study is directly relevant to the goals of the Emerging Worlds solicitation to understand the formation and early evolution of the Solar System and the strategic question of learning How did the Sun s family of planets, satellites, and minor bodies form and evolve?

We will utilize a coordinated approach where the UCLA ion microprobe will be used as a reconnaissance tool for selecting suitably ancient lunar zircons by in situ U-Pb dating. This can be accomplished with consumption of only a few nanograms of zircon, thereby preserving the remainder of each sample for high-precision, high-accuracy U-Pb isotopic analyses by thermal ionization mass spectrometry at Princeton University. For this work, samples will be annealed and then chemically abraded to provide crystallization ages of pure zircon domains without confounding ages affected by Pb-remobilization due to metamictization or structural damage from impacts. The same sample solutions will then be measured for Hf isotopic compositions utilizing inductively-coupled plasma mass spectrometry (ICPMS) at Princeton and at UCLA. All relevant Hf isotopes will be determined with high precision and high accuracy, and potential cosmogenic isotope shifts will be monitored. The resulting data will be considered in a model of Lu-Hf isotopic evolution by using recently determined solar system evolution parameters based on the analyses of large zircons separated from the Agoult eucrite meteorite (Iizuka, Hibiya, and Amelin, 2015 LPSC, #1602). The timing of separation (closure age) of the KREEP reservoir on the Moon, the signature of which is carried in the zircon Hf isotopes, from the chondritic evolution curve will thereby constrain the crystallization time of the Lunar Magma Ocean.

Nielsen, Sune/Woods Hole Oceanographic Institution
Using Vanadium Isotope Ratios to Investigate the Source Material of Earth, Moon and Mars

The nature and origin of the material that accreted to form the Earth and Moon has been and continues to be one of the most fundamental questions in cosmochemistry and planetary science. Most models of the composition of the Earth rely on the fact that the relative abundances of the refractory lithophile elements in the silicate Earth are almost identical to that of carbonaceous chondrites, which led to the hypothesis that Earth is largely built from a mixture of the various types of chondritic meteorites that we currently have in our collections. In recent years this traditional view of an entirely chondritic Earth has been challenged by the emergence of several isotopic tracers that have shown the silicate Earth and chondrites to be systematically different. However, it is not clear if some of these isotopic anomalies can be explained by core formation or other hidden reservoirs within the Earth that could produce an overall chondritic bulk Earth.

A significant portion of Earth accretion likely took place via the formation of the Moon in an impact with another planetary body. As such the accretion history of Earth is intimately linked to the Moon and with the emergence of many new isotopic systems the origin and composition of the Earth-Moon system has been studied intensely. Perhaps the most interesting observation arising from these new isotopic data is that the silicate Earth and Moon, for all elements so far investigated, are isotopically indistinguishable. This observation is interesting because the impactor is expected to have been isotopically distinct from the proto Earth for several elements.

In a paper published in February 2014 we showed that the stable vanadium isotope composition of bulk Earth is different by about 10 to all meteoritic material so far investigated, which include carbonaceous and ordinary chondrites as well as achondrites from the HED parent body and the Martian meteorite Nakhla. These data therefore support the notion that Earth contains at least a portion of non-chondritic matter. Additionally, since Earth is so anomalous in vanadium isotopes, it is expected that the Moon-forming impactor would not carry an identical vanadium isotope signature to proto-Earth. Therefore, the vanadium isotope composition of the Moon may provide a test of the giant impact hypothesis.

Vanadium isotopic variation in the Solar System is potentially linked to early irradiation because 50V may be produced via spallation reactions. Here we propose to perform three separate vanadium isotope studies designed to elucidate the causes of vanadium isotopic variation observed in meteorites and link these to accretion processes of the Earth, Moon and Mars. The first project investigates V isotopic variation in CAIs from Allende. The vanadium isotopic data for bulk CAI powder will be complemented by an investigation of initial 10Be abundances in the same CAIs determined via SIMS measurements of boron isotope compositions. Beryllium-10 is the best and most convincing recorder of early Solar System irradiation and if V isotope variation was due to irradiation we would expect the abundance of 10Be to correlate with V isotope compositions. The second project entails an investigation of the V isotope composition of bulk silicate Mars and the Moon. These data will provide a new test for the giant impact hypothesis by examining if the Earth and Moon are identical in V isotopes. The Martian V isotope data will show if Mars, like Earth, is distinct from chondrites and give additional clues about the accretion history of Mars and the origin of V isotope variation in the Solar System. The third project aims to characterize the V isotope compositions of all major groups of chondrites not already investigated in our previous study. These measurements will determine if the V isotopic offset between silicate Earth and chondrites is consistent and hence if Earth could have accreted entirely from chondritic material.

Nittler, Larry/Carnegie Institution of Washington
Acquisition of a high-brightness, high-spatial-resolution oxygen ion source for the Carnegie NanoSIMS ion microprobe.

We request Planetary Major Equipment funds to partially support the purchase of an RF plasma ion source to replace the current duoplasmatron as a source of negative oxygen primary ions on the Cameca NanoSIMS 50L ion probe at the Carnegie Institution of Washington. Additional matching funds will be provided by the Carnegie Institution. This source has several major advantages over the decades-old duoplasmatron technology, most notably a substantial increase in brightness, allowing for a factor of ten increase in beam density and four-fold improvement in spatial resolution, as well as improved stability. Although the spatial resolution of NanoSIMS measurements with the Cs+ primary ion beam is typically of order 100 nm, measurements of electropositive elements (e.g., Mg, Ca, Ti, Fe, &) require an O- beam, with a typical resolution of several hundred nm for the duoplasmatron source. In contrast, the proposed RF plasma O- source routinely achieves a resolution and beam density comparable to the NanoSIMS Cs source, expanding the scientific potential of the instrument. The new source will greatly enhance existing scientific investigations of the proposers currently funded by grants from the Cosmochemistry and Origins of Solar Systems programs (predecessors of the Emerging Worlds program) as well as other programs (LARS, SSERVI) and enable new science highly relevant to the goals of NASA s Planetary Science Division. Specific applications of the new source relevant to existing grants include 1) spatially-resolved measurements of Cr isotopes in <100-nm spinel grains to better characterize the carrier of 54Cr anomalies in bulk meteorites; 2) spatially resolved measurements of Mg, Ca, and other isotopes in situ in sub-micron presolar silicate grains; 3) Ti-, Fe- and Ni-isotopic measurements of sub-micron presolar SiC grains and internal sub-grains within presolar graphite grains; 4) high-resolution D/H measurements of hydrous phases in interplanetary dust particles (IDPs); 5) Al-Mg measurements in sub-micron Al-rich grains from comet Wild-2; and 6) trace element measurements in small lunar volcanic glass beads and melt inclusions for which D/H and volatiles are measured. Additional applications directly relevant to NASA s goals include measurement of the Al-Mg and Mn-Cr systems in small grains within chondrules, CAIs, chondritic matrices, and IDPs, boron isotopes in lunar glasses and melt inclusions, and depth-profile measurements of solar-wind implanted in Genesis mission substrates.

Simon, Steven/The University of Chicago
Petrologic, Isotopic, and Chemical Aspects of the Origin of the Solar System

The proposed work consists of petrographic, mineral-chemical, and XANES (X-ray absorption near-edge structure) analysis of pristine and low-grade ordinary and CO chondrites and experimental run products, and sample selection, petrographic support and sampling for isotopic studies of meteoritic material. Some of this work is a continuation of studies from NASA grant NNX13AE73G, Chemical Aspects of the Origin of the Solar System (L. Grossman, PI; S. Simon, Co-I).
The study of chondrites consists of two tasks. (1) Our study of refractory inclusions (CAIs) in two pristine CO3 chondrites suggested that an Acfer 094-like subgroup of CO3 chondrites might exist. To see if this is true, the CAI populations in additional CO3s, such as MIL 05024, 090470, and 090010 will be documented. New and unusual inclusion types will be thoroughly studied and reported. If a subgroup is identified, the classifications will be followed up with a TEM study of their matrices by Collaborator Brearley to see if the distinctions extend to that component of the samples. (2) Low-grade chondrites are identified and assigned grades on the basis of where analyses of ferroan olivine in a sample fall on a plot of Ã-Cr2O3 vs. mean wt% Cr2O3. Despite the importance of this parameter, neither the valence of Cr nor what phase or phases it enters as it responds to metamorphism are known. Therefore, a combined petrologic/TEM/XANES study (with Collaborators Brearley and Sutton) of low-grade (3.0 3.2) chondrites is proposed, to determine the valence of Cr in them and its response to the onset of metamorphism, improving our understanding of the redox conditions under which chondrules formed and were metamorphosed. Experimental study of redox kinetics continues work with Collaborators Sutton, Beckett and Stolper in which we are attempting to understand the presence of Ti3+ and Fe2+ in chondrule olivine and pyroxene. In the next generation of experiments, partially molten, reduced starting materials will be cooled at various rates applicable to chondrule formation in a relatively oxidizing atmosphere in which the oxidizing species are diluted with an inert gas (Ar) to simulate nebular partial pressures. In a companion set of runs, partially molten, oxidized starting materials will be cooled under reducing conditions. The valences of Ti and Cr will be determined by XANES. The PI will select and characterize samples for three isotopic studies. (1) With Collaborators Bouvier, Kita and Tenner, chondrules will be studied and their absolute (Pb-Pb) and relative (Al-Mg) ages determined. (2) With Collaborator Krot, O-isotopic compositions and Al-Mg relationships of grossite-bearing CAIs will be determined, to improve the isotopic database for that inclusion type. (3) With Collaborator J. Simon, the Mg and Ca or Ti isotopic compositions of rims on refractory inclusions will be measured in order to distinguish between evaporative or depositional origins.
Methods: Electron and X-ray microbeam techniques will be used to study the samples (FIB and polished thin sections). Selected areas will be documented by scanning electron microscopy (SEM); mineral compositions determined by electron microprobe (EMP); valence and coordination of Ti and Cr by XANES; and most isotopic analyses by MC-ICPMS and SIMS.
Relevance: This program solicits proposals related to understanding the formation and early evolution of our Solar System. Task 1 will yield new information on very early Solar System materials (chondrules and CAIs) and early evolution of chondrite parent bodies. Task 2 will improve our understanding of chondrule precursor assemblages and the environments and processes to which they were subjected. Task 3 will improve our understanding of the timing of chondrule formation; the distribution of 26Al and 16O in the early Solar System; and the formation of rims on, and transport of, refractory inclusions in the solar nebula. All tasks are relevant to the Emerging Worlds program call.

Stroud, Rhonda/Naval Research Laboratory
Mircometer to Picometer Scale Microscopy of Primitive Solar System Materials

We propose to address fundamental outstanding questions regarding the provenance of carbonaceous phases in the early solar system through state-of-the art transmission electron microscopy (TEM) studies: (1) How and where did meteoritic nanodiamonds form? (2) Are the majority of primordial planetary gases (Q-gases) carried by a single phase or polymorph of carbon, or multiple phases? (3) How do presolar SiC grains from different stellar sources form, and how are they preserved in the interstellar medium and solar nebula to be incorporated into comets and asteroids? The majority of prior work on these phases has been conducted on samples prepared as acid-resistant isolates from primitive meteorites. With PRISM, a newly installed aberration-corrected scanning transmission electron microscope at the Naval Research Laboratory, we can reexamine the well-studied residue samples with single-atom sensitivity, to reveal previously unobservable features, including minor and trace element contents, and structure of carbonaceous phases down to single carbon sheets. Correlated with bulk noble gas data, these atomic-scale studies will allow us to determine whether residues with different noble gas contents show different microstructural characteristics, e.g., more or less amorphous carbon in nanodiamond residues or variations in carbon nanostructure in phase Q residues, to better constrain the phase formation and processing histories. Studies of presolar SiC as grain separates will enable correlation of crystal structure and subgrain content with stellar progenitor sources, and for X grains from supernovae, allow us to examine the effects of in situ decay of extinct radionuclides like 26Al on the crystal structure. In addition to studies of residue samples, we plan in situ measurements of nanodiamonds and presolar SiC in focused ion beam and microtomed-prepared sections of meteorites and interplanetary dust particles. It is already known that at least some populations of nanodiamonds are spatially associated with insoluble organic matter in meteorite matrices. We seek to better understand the chemistry and structure of the organic matter spatially associated with nanodiamonds to determine if there is any genetic link or common processing history. In situ studies of presolar SiC grains will offer the opportunity to look at the very outer surfaces of the grains, to identify signatures of radiation processing, ion implantation, and/or oxygen plasma processing that reveal important information about the interstellar and nebular histories of the grain. If a unique Q carrier is identified in residue samples, we will also search for this phase in situ where possible. Completion of the proposed studies will, without question, provide new insight into the origin of nanodiamonds, the nature of the Q-carrier phase(s), and the formation and survival of presolar SiC, greatly enhancing our understanding of the provenance of carbonaceous phases in primitive solar system materials.
This work addresses the Emerging Worlds goal stated in C2 of the ROSES: to conduct scientific investigations related to understanding the formation and early evolution of our Solar System. Specifically, this proposal addresses the physics and chemistry of events and materials that are relevant to & the formation of minor bodies, including dust, and to the early history of these bodies.

Taylor, Susan/US Army Cold Regions Research and Engineering Lab
Sampling Comet Dust from Antarctic Air

Information on the composition of the proto-solar nebula dust and gas that collapsed to form our solar system can only be gleaned by studying primitive materials those that have not been severely altered by thermal or aqueous processes. Comets derive from distal regions of the Solar System and, having not been heated by the Sun or reprocessed into large bodies, are thought to contain samples of the primitive materials from which our solar system formed. We propose to collect particles thought to be from comets and analyze them to learn more about the solids condensed from the nebula and the structure of primitive organics they contain. We will collect the particles by suctioning and filtering clean air at South Pole Station, Antarctica.

Analyses of interplanetary dust particles (IDPs) collected in the stratosphere by aircraft have shown that some of these particles, the chondritic porous IDPs (CP-IDPs), are indeed primitive materials. They contain vapor-deposited minerals, silicates formed under a range of redox conditions including very reducing ones, glasses with embedded metal and sulfides (GEMS), and abundant organic matter. These components also include interstellar materials and both high and low-temperature nebular solids. The main impetus for the Stardust space mission was to return for analysis bona fide samples from the comet Wild 2. Recently, particles indistinguishable from CP-IDPs (Noguchi et al. 2015), and rare, ultra-carbonaceous micrometeorites (Duprat et al. 2010) were collected from melted Antarctic snow.

There are several advantages to collecting IDPs directly from clean Antarctic air. We can collect an order of magnitude more particles for a fraction of the cost of collecting IDPs in the stratosphere. Timed collections, targeted to collect materials from specific meteor streams or linked to seasonal variations in the particle flux, require only changing the filters. Air filtering avoids having to collect and melt large volumes of snow, improves temporal resolution, and eliminates particle contact with water during collection. Avoiding contact with melt water increases the possibility of preserving interesting water-soluble or easily altered phases.

Our proposed IDP collector will use isokinetic sampling and filtering of the very clean air stream at South Pole to collect 300 900 IDPs per month (size range 5 50 ¼m) based on measured stratospheric IDP concentrations (Brownlee et al. 1977, Zolensky and Mackinnon 1985). Background aerosol concentration at South Pole is low in the > 3¼m size range, and the intake will be a few meters above the surface to minimize snow entrainment and permit year-round collection.

For this work, we will catalogue extraterrestrial particles on the filters, analyze the isotopic, chemical, and elemental compositions, and describe the microstructure of representative samples. The samples will likely originate from many objects, allowing us to expand our knowledge of these primitive materials. By time-stamping the collections, we expect to link the particles with specific meteor streams. By studying the organics that also have high deuterium values, we expect to learn more about the cold, outer regions of the planetary disk. This new collection will be a valuable resource for the extraterrestrial-materials research community, which is currently sample-limited for primitive materials.

The Emerging Worlds Program's stated goal is to understand the formation and early evolution of the Solar System and includes sample-based studies of extraterrestrial materials. The proposed work is relevant to this NASA call as it aims to collect and study large numbers of pristine, primitive, extraterrestrial materials whose compositions and microstructures will provide insight into conditions that existed early in the formation of the Solar System. It will also provide data on the types and flux of organic molecules arriving on Earth.

Villanuev, Geronimo/NASA Goddard Space Flight Center
A Deep Search for Organic Species and their Isotopic and Isomeric Signatures in Comet

Comets are cryogenically preserved relics from the early solar system. Exploring their composition is directly relevant (1) to understanding the origins of our planetary system and (2) to testing the hypothesis that small icy bodies have delivered prebiotic matter to early Earth. This proposal provides frontier advances in both areas by focusing on three possible cosmogonic indicators: isotopic ratios, nuclear spin temperatures (derived from isomeric abundance ratios) and chemical abundances. These indicators reveal information about the prevailing temperatures, abundances and radiation fields in the early Solar System, 4.6 billions of years ago. Decoding these clues is critical. The infrared CH-stretch region (3.2 - 3.6 μm) is the prime spectral region for sensitively sampling the organic composition of comets through their solar pumped fluorescence spectra. In the last decades, we acquired an extensive observational database of emission lines in this region from comets, obtained with state-of-the-art spectrometers at world-class observing facilities, notably (since 1999) with the powerful cross-dispersed NIRSPEC at Keck II; while in recent years, we have greatly improved our ability to analyze these spectral features, thanks to our advanced data processing routines and realistic quantum band models. The proposed work will permit us to apply these new techniques to our rich archival dataset, in which we find many unidentified spectral features. Some of these lines match the locations of spectral lines of C2H5D (deuterated ethane) and C3H8 (propane), reported by laboratory experimenters. As importantly, our new molecular models now allow us to retrieve accurate spin temperatures for C2H6 (ethane), CH3OH (methanol) and CH4 (methane). We propose to:

• Extract ultra-high fidelity calibrated cometary spectra in the 3.2 - 3.6 um wavelength range from our rich database of 20 comets acquired over 15 years using high-resolution spectroscopy. With these ultra-high fidelity spectra:

• We will use our modern quantum band models to measure improved abundance ratios and nuclear spin temperatures for C2H6, CH3OH and CH4 for our full sample of comets. For C2H6 and CH3OH the latter will be pioneering measurements.

• We will also perform sensitive searches for mono-deuterated ethane, by developing a quantum model for the ν7 band of C2H5D that will address features in our spectra.

• We will develop a semi-empirical line list for C3H8 that will allow its clear identification and quantification, thereby establishing the abundance ratios of the main homologous series of saturated hydrocarbons (CH4, C2H6 and C3H8) and also testing their production relationship. In summary, we will determine accurate molecular abundances for four key organic species (CH3OH, CH4, C2H6, and C3H8), retrieve the D/H ratio in ethane, and measure spin temperatures for cometary hydrocarbons. The proposed work is highly relevant to the Emerging Worlds program because it targets advanced knowledge of the chemical and isotopic properties of cometary material – remnants from the Solar System's formative stages.

Walker, Richard/University of Maryland
Siderophile Element Studies of the Formation and Early Evolution of the Solar System

Goals and objectives: The primary goals of the proposed work are to constrain the timing of, and processes by which certain important early Solar System events occurred. We also seek to constrain the proportions and provenance of materials involved in these processes. Our contributions to these topics will be achieved primarily via the analysis and interpretation of siderophile element abundances and isotopic compositions. Siderophile element tools to be used include the short-lived 182Hf-182W and long-lived 187Re-187Os isotopic systems, nucleosynthetic variations in the isotopic compositions of Ru and Mo, as well as the measurement and modeling of abundances of the highly- and moderately-siderophile elements (HSE: including Re, Os, Ir, Ru, Pt, Pd; MSE: including Mo and W). Proposed major tasks include:

1) Application of the 182Hf-182W system to three sub-tasks using our techniques to measure 182W/184W at a precision of <5 ppm (2SD). One subtask will be to refine and expand our knowledge of metal-silicate segregation ages of early Solar System bodies as recorded in iron meteorites. Current measurement capabilities, coupled with the application of the Os cosmic ray exposure dosimeter will permit resolution of relative segregation ages of <1 m.y. Targets of this aspect of study will include the IIF, IIE, IIG and IIIF iron meteorite groups, as well as ungrouped irons. A second task will be to examine the thermochronology of H chondrites through examination of the Hf-W isotopic systematics of metals and silicates present in these meteorites. A third subtask will be to use the 182Hf-182W and HSE systematics of lunar basalts to further examine formation mechanisms for the Moon, as well as to place improved constraints on the minimum possible age after Solar System formation for lunar magma ocean crystallization.

2) Conduct isotopic (Ru, Mo) analysis of bulk chondrites. The goals of this task are to further explore the isotopic characteristics and proportions of diverse pre-solar materials incorporated in bulk chondrites. Comparison of the nature of the anticipated anomalies with the chemical characteristics of the parent body may allow important inferences to be made regarding the selective survival of diverse pre-solar materials incorporated into different chondritic parent bodies.

3) Continue our longstanding study of the origin and chemical evolution of metals in the parent bodies of magmatic, non-magmatic, and ungrouped irons, emphasizing genetic constraints obtained from Ru and Mo isotopic compositions, as well as the modeling of HSE. The goals of this work are to provide an improved understanding of metal segregation and crystallization processes in differentiated bodies, and also constrain the isotopic and chemical variations present among the parent bodies of these meteorites.

Methodology: We will use proven techniques for precisely measuring siderophile element abundances and isotopic compositions using thermal ionization mass spectrometry and inductively-coupled plasma mass spectrometry.

Relevance: All of the proposed work is directed towards the stated objectives of the goals of the Emerging Worlds program which aims to understand the formation and early evolution of the Solar System , and address the question "How did the Sun s family of planets, satellites, and minor bodies form and evolve?" (page C.2-1, ROSES 2015).

Watson, Heather/Rensselaer Polytechnic Institute
Diffusion in iron-nickel alloys and sulfides: Constraints on segregation and crystallization of early planetary cores

Science Goals and Objectives: Iron meteorites are considered to be remnant cores of early differentiated planetesimals. The segregation of the iron core from the silicate mantle, and the eventual cooling and crystallization of the metallic core are chemically recorded in the metals and sulfides that comprise the meteorites. Recent evidence suggests that some iron meteorites may have differentiated and cooled very early in the solar system s history (before chondrites), and they were larger than previously thought (up to 1000 km). The goals of this study are centered around the theme of providing experimentally derived diffusion data in relevant systems that may aid in constraining the timing of core segregation, crystallization, and cooling in these planetesimals.

1) Pb in sulfides: Absolute ages have been measured by Pb-Pb dating of troilite (FeS) nodules in iron meteorites. This, in conjunction with established cooling rates and age of core segregation, provides constraints on the timing from accretion and differentiation through crystallization and final cooling. Limited data on Pb diffusion in sulfides precludes using an accurate closure temperature for this system; proxies such as the closure of Os in pyrite have been used but may not be realistic. Experiments are planned to measure Pb diffusion in FeS with direct applicability to the closure temperature of Pb in this system.

2) Ag sulfides and Fe-Ni alloys: The Pd/Ag isotope system is frequently used to date the age of crystallization of iron meteorites. The closure temperature, at which the isotopic signature is considered to be "locked-in" is not well constrained. Experiments are proposed to determine the closure temperature in the main phases of iron meteorites (specifically Fe-Ni alloys and FeS).

Methodology: Diffusion experiments will be conducted in the experimental geochemistry laboratory at Rensselaer Polytechnic Institute (RPI) in sealed silica tubes in 1 atm furnaces, and in the piston cylinder apparatus. Experiments will be analyzed using a combination of electron microprobe and laser ablation ICP-MS at RPI, Rutherford backscattering (RBS) techniques at Ion Beam Laboratory at the University at Albany. The experimental data will be used in conjunction with analyses on natural meteorites, as well as literature data to model constraints on the timing of core formation, crystallization and cooling in iron meteorite parent bodies.

Relevance: The proposed work is relevant to the Emerging Worlds program element in the area contributing to understanding the formation and early evolution of our Solar System& the physics and chemistry of events and materials that are relevant to the formation of planets, satellites, and minor bodies& . In particular, this work relates to understanding the processes that contribute to core formation and evolution in planetesimals, and the retention of the chemical signatures from these processes in iron meteorites.

Westphal, Andrew/U. C. Berkeley
Diversity of primitive bodies from oxidation states of transition metals

Here we propose to study the chemical and isotopic properties of ancient solar system materials, including primitive meteorites and IDPs, and compare their formation conditions and early evolution with samples of comet Wild 2. We propose to carry out two independent studies.

In Project 1, we propose to translate recent quantitative Ti and V K-edge oxygen barometers to L2;3 XANES/EELS in order to

-- investigate redox heterogeneities of individual fine-grained (100 nm) spinels in primitive solar-system materials using Ti, V, Fe L2;3 XANES
-- derive quantitative oxygen fugacity where no oxybarometric mineral assemblage is present
-- derive Ti, V, Fe oxidation state and site occupancy in spinel group minerals
-- derive quantitative oxygen fugacity, with explicit P,T constraints

We will publish a new L2;3-edge spinel oxybarometer, which will apply to L2;3 spectra acquired in transmission using Scanning Transmission X-ray Microscopy (STXM) or Electron Energy Loss Spectroscopy (EELS), and on surfaces using Total Electron Yield (STXM or Photoemission Electron Microscopy, PEEM). We will focus on spinel group minerals, whose cubic structures result in X-ray absorption spectra without polarization effects, in contrast to minerals such as pyroxene. Spinel group minerals (magnesiospinel, chromite, ulvöspinel, magnetite) are ubiquitous in meteorites, with wide-ranging compositions reflecting different redox formation conditions and contain multivalent metals in either tetrahedral or octahedral cation site occupancies. We will prepare a suite of spinel standards at known oxygen fugacity at JSC. We will determine the standards cation site occupancies using EXAFS and ALCHEMI, and oxidation states (Ti, V, Fe K-edge XANES) in order to calibrate Ti, V, Fe L2;3 STXM, PEEM and EELS spectra, which are highly sensitive to both oxidation state and structure. We will investigate the diversity of redox conditions in Allende and Vigarano meteorite samples, which have previously been characterized by microXRF at the Australian Synchrotron XRM beamline. These meteorites contain undifferentiated, primitive solar system materials, which retain a record of the redox environments of the early forming solar system in which they formed. We will utilize very large high-resolution XRF maps to identify Ti-spinel phases and candidate oxybarometric mineral assemblages. We will employ three oxybarometric techniques to verify our results: (1) analysis of the composition of mineral assemblages by microprobe; (2) Ti, V K-edge XANES oxybarometers; (3) newly calibrated Ti, V, Fe L2;3 XANES.

In Project 2, we propose to quantitatively explore the diversity of comets by measuring the oxidation state of Fe, with an emphasis on the metal content; the crystalline silicate fraction; and the isotopic composition of O in Chondritic- Porous Interplanetary Dust Particles. We will carry out these studies using synchrotron X-ray and ion microprobes at the Advanced Light Source at Lawrence Berkeley National Laboratory, and the Cameca ims1280 at the University of Hawai i, respectively. These results can be compared directly to cometary samples of Jupiter-family comet 81P/Wild 2, the only samples from a known comet.

Willacy, Karen/JPL

The comet/disk connection: Volatile formation in protostellar disks and the observed composition of comets

Comets are primitive icy bodies left over from the early solar system. They spend most of their lives in one of two reservoirs - the Oort cloud or the Kuiper Belt - until perturbed into an orbit that brings them close to the Sun. These reservoirs are very cold, so the original compositions at formation are largely preserved. Thus comets uniquely trace conditions and processes in the early outer solar system. The great diversity in composition observed among the comets reflects a diversity in their formation conditions. Comparing comet measurements with models of the protosolar nebula can provide insights into the origins of the comets and the rest of our planetary system.

We propose to investigate the chemical and physical processes behind the observed cometary abundances. We will explore the signatures that the protosolar nebula's initial chemical composition, thermal structure, radiation fields and time evolution left in the volatile ices deposited during comet formation. For each nebula model in an extensive set, we will compare the ices' compositions in detail with observations of individual comets. A large and rapidly growing number of such observations is in hand. We will thus constrain the conditions under which the various molecules in any given comet can have formed. Comets may be comprised of molecules that were formed in different environments and transported to the comet formation region, and understanding where and when various molecules can have formed will help us constrain the degree to which the condensates were carried from place to place before the comets' assembly. Our modeling will therefore cover the transport of materials from different regions of the nebula and their coming together to make individual cometesimals at locations across the comet-forming region.

Our main objectives are to establish
1. The main chemical pathways that led to the synthesis of cometary volatiles,
2. Which processes in the protosolar disk have left strong signatures in the cometary ices, and
3. The origins of the chemical diversity observed in the comets.

All three address key issues in the solar system's origins. Newly detailed observations of comets' molecular makeup are available from the Rosetta mission and the Atacama Large Millimeter Array. Interpreting the data in light of protosolar nebula models has largely been limited to qualitative discussions, and further progress requires a more quantitative approach. Nebula models have mainly been compared with gas column densities measured in other protostellar disks, and there has been no systematic comparison of predicted midplane ice abundances with individual comets. The diversity of observed comet compositions indicates divergent histories even for bodies now on similar orbits, and matching them with nebula modeling will enable us to explore which parameters lie behind this variation. Work of the kind we propose is essential if comets are to become as valuable as meteorites in telling us about conditions in the early solar system.

Woon, David/University of Illinois at Urbana-Champaign
Quantum chemical studies of organic chemistry in protostellar nebulae

OBJECTIVES. Volatile compounds, both organic and inorganic, coevolved with refractory materials during the emergence of our Solar System from its protostellar disk and were incorporated into the host of bodies that populate our system, from dust through planets. The chemical evolution of volatiles can be observed directly in protostellar nebulae present around us in the galaxy, providing insight into primordial processes in our own Solar System, where we are restricted to studying ancient relics that have been subjected to continued energy processing that can mask the original chemistry. We propose to continue our theoretical studies of the chemistry of volatile organic compounds occurring in protoplanetary disks or in the interstellar medium from which disks condense. Our first objective is to characterize plausible chemical pathways that can function efficiently at temperatures below 100 K to form or alter chemical compounds on or within icy grain mantles that accrete on refractory dust. Our second objective is to predict vibrational and electronic spectra of compounds formed in ices via these reactions in order to provide predictions that would serve to verify our pathways through suitable experiments. The specific reactions we propose to study will involve low-energy deposition of various cations on ices of various compositions. The reacting cations of interest include C+, CH3+, N+, CHn+, OH+, and others. In addition, we propose to study the reactions of small compounds containing Si and C such as SiC in water ice to investigate if co-formation of organic compounds and oxygenated silicon compounds can occur in icy grain mantles.

METHODOLOGY. Quantum chemical calculations at various levels of theory will be used to characterize chemical pathways and spectroscopic properties of product and intermediate compounds, including both vibrational and electronic spectra. For smaller systems, coupled cluster methods such as CCSD(T) will be used, in part to benchmark density functional theory (DFT) calculations that must be used for larger calculations. We will use B3LYP and other functionals such as wB97X-D for treating ices that will be modeled with large cluster calculations using DFT. We routinely perform calculations with clusters up to ~20 chemical entities, which we have shown to be of sufficient size to predict both the vibrational and electronic spectra of amorphous water ice. We will use small correlation consistent basis sets, which we have shown to be superior to Pople-style basis sets but do not incur significant additional computational costs. Electronic spectra will be characterized with time-dependent density functional theory (TDDFT).

SIGNIFICANCE. Identifying compounds that can form in protostellar disks is relevant to the general objective of the Emerging Worlds program to understand the formation and early evolution of our Solar system& The physics and chemistry of events and materials that are relevant to the formation of planets, satellites, and minor bodies& is covered by the program. Specific areas that are of interest to the program that would be addressed by the proposed work include: (i) Chemical and physical processing of gas, dust, and ice ; and (ii) Formation of organic molecules in space. Theoretical studies such as this one are explicitly supportable by the program.

Yin, Qing-zhu/University of California at Davis
Establishing Planetary Genealogy of Emerging Worlds

Isotopic signatures, in particular those of nucleosynthetic origin from dying stars that contributed matter to the nascent solar nebula, are likened to DNAs for the emerging planetesimals in the early Solar System. The new data we are gathering now allow us to pinpoint the spatial provenance of planetary

materials, to fingerprint genetic relationships of every newly discovered meteorite with known planetary materials or to establish hitherto unknown new planetary objects and groups.
Centered around our new analytical capabilities developed at UC Davis, we have recently investigated the utility of using nucleosynthetic isotopic anomalies of Cr and Ti as fingerprints for establishing planetary genetics of common chemical reservoirs among a range of planetary materials (Sanborn et al., 2014, 2015; Williams et al., 2015). The approach has proven to be a highly effective and diagnostic when used in conjunction with other geochemical parameters such as □17O, as shown by a range of recent publications and conference reports. The investigations ranged from establishing meteoritic identities of recent falls and finds (Jenniskens et al., 2012, 2014; Popova et al., 2013; Ash et al., 2014), studies of anomalous eucrites beyond Vesta (Benedix et al., 2014; Sanborn and Yin 2014, 2015), deciphering source composition of unique ungrouped achondrites of allegedly Hermian origin (Sanborn et al., 2013, 2014; Irving et al., 2014; Kita et al., 2014), leaching carbonaceous chondrites to establish multiple end-member components in the solar nebula (Yamakawa and Yin, 2014), strengthening the case for the differentiated planetesimals with chondritic crusts with partial melting of the CV/CK and CO parent bodies (Sanborn et al., 2015, Elkins-Tanton et al., 2011), as well as establishing genetic links among the CR1, CR2, CR3, CR6, CR7 groups of primitive carbonaceous chondrites, metachondrites, and differentiated igneous achondrites (Sanborn et al., 2014; Irving et al., 2014).

We propose to expand our investigation into a wider range of planetary materials (e.g., iron meteorites and pallasites) with our established procedures for measuring μ54Cr to shed new light on their complex petrogenetic relationships. We also propose to extend the investigation to Ti from the same suite of samples used for Cr isotope investigation to elucidate the evolving chemical reservoirs and their interconnection in the emerging worlds with an added new dimension (e.g. Warren et al., 2011; Williams et al., 2015). The fractions used for μ54Cr studies were all saved for future Ti and other suitable isotope systematic studies (e.g., Fe, Zr).

In synergy with the efforts using isotopic anomalies as a forensic tool to establish planetary genealogy, we have been actively developing new analytical capabilities, namely a modern high-precision isotope dilution thermal ionization mass spectrometry technique for U-Pb dating of extraterrestrial materials. Our goal is to establish a comparative chronology of short-lived 26Al-26Mg and 53Mn-53Cr systems anchored to the long-lived U-Pb clock, in order to provide key observational constraints for understanding rates of accretion and differentiation processes in the early solar nebula. Using the survey technique developed in PI s laboratory for measuring Mg isotopes in calcium-aluminum-inclusions (Tollstrup et al., 2011, Wimpenny et al., 2014), we have identified a suite of CAIs with negative ´25Mg that are likely to have most variable 235U/238U ratios. We propose to extend our measurement of ´25Mg to ´235U, μ54Cr, μ50Ti and determine the absolute U-Pb ages and relative 26Al-26Mg and 53Mn-53Cr ages on individual CAIs.

The proposed research is highly relevant to NASA s Emerging Worlds program as it addresses directly the fundamental science question of how the Solar System formed and evolved from planetary materials perspective. It also proposes to solve key questions with major interdisciplinary efforts from diverse expertise.