



Identifying Planetary Mixed Materials Through In Situ Mass Spectrometry

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Objectives: A wide range of planetary and astrophysics mission science cases require characterizing interplanetary, circumplanetary, and interstellar dust. We aimed to strengthen mission proposals in these areas by demonstrating the ability to measure dust particles' compositions with the next generation of impact-ionization time-of-flight mass spectrometers, successors to Cassini's Cosmic Dust Analyzer (CDA) and Europa Clipper's Surface Dust Analyzer (SUDA). Two key objectives were to (1) quantify the instruments' precision in measuring elemental ratios, and (2) show that diverse planetary materials can be identified from mass spectra at the expected instrumental resolutions and noise levels.

Background: In impact-ionization instruments, the incoming dust particle strikes a target plate made of a metal of low cosmic abundance, such as gold or platinum. The impact converts the particle and a tiny patch of the plate into a plasma. Typically, plasma electrons and negative ions are collected on the target, while positive ions are accelerated into an ion detector by electric fields set up in the instrument. Lighter ions accelerated in the same electric field reach the detector faster, yielding a time-of-flight mass spectrum.

Prototype instruments can be tested under space-like conditions in a large vacuum chamber, where an electrostatic field accelerates micron-sized and smaller particles to orbital speeds. The accelerator is operated by the partners at the University of Colorado (<http://impact.colorado.edu>) through a cooperative agreement under NASA's Solar System Exploration Research Virtual Institute (SSERVI).

The steps in testing an instrument include grinding particles of each material of interest to the appropriate size range, determining the particle-to-particle composition variations so these can be separated from instrumental effects, and coating each particle with a thin layer of a conductor such as aluminum, copper, or polypyrrole, so it can be charged and electrostatically accelerated into the instrument in the vacuum chamber.

Approach and Results: The most important results of the two-year project were:

- Graduate student Zachary Ulibarri earned his PhD from CU with the project's partial support. He was considered for a postdoctoral position in the Europa Clipper team at JPL and is now a researcher at Cornell University.
- Developed procedures for grinding various materials using new planetary ball mill, into particles in the micron size range that can be accelerated to orbital speeds in the laboratory. This replaces a process that involved shipping the materials to a facility in Germany where scheduling was a perpetual issue.
- Developed a device for vapor-depositing thin metal coatings on dust particles to enable electrostatic charging and acceleration in the laboratory vacuum chamber. This evaporative coating process replaces wet-chemistry methods that have a significant failure rate and involve toxic solvents, whose residues have sometimes contaminated laboratory mass spectra.
- Characterized the compositions of reference materials including San Carlos olivine and anthracene down to the scale of individual micron-sized dust particles, using energy-dispersive X-ray spectroscopy in two independent laboratories. Obtained mass spectra of these reference particles in the accelerator using the Hyperdust instrument. The olivine results show that the instrument's intrinsic uncertainty in elemental ratios such as Mg/Si and Fe/Si is less than a factor two. Efforts to further reduce this uncertainty by optimizing the amplifier gain and other instrument parameters, and to publish the findings in a refereed journal will continue past the end of the funding period.
- Identified and acquired potential new dust sources, including organometallic species such as ferrocene, which may be used to further illuminate instrumental uncertainties in the elemental ratios. These species will be tested once the grinding process has been refined.
- Created synthetic model spectra for over two dozen minerals, using as a basis the mass spectra from the accelerator and a now-decommissioned facility at the Max Planck Institute for Nuclear Physics in Germany. These model spectra include realistic noise and mass line shapes specific to impact-ionization instruments. The noise parameters of the synthetic spectra can be tuned to match current and future instruments including Clipper-SUDA, IMAP-IDEX, and Hyperdust.
- Demonstrated automated identification of a subset of the synthetic mass spectra, and its dependence on signal-to-noise ratio. These results will be expanded to a broader set of minerals and published in the refereed literature after the end of the funding period.
- Towards creating sub-micron-sized dust particles of mixed but well-defined compositions, created aluminum particles with a partial gold coating that can accept self-assembling monolayers of thiol-bearing organic molecules. This may allow for acceleration of dust particles bearing complex organics, including amino acids, which would also greatly strengthen proposals for dust instruments for icy ocean world missions.

Significance/Benefits to JPL and NASA: *In situ* mass spectrometry of solid particles is a key measurement technique for missions targeting airless bodies' surface compositions (Europa Clipper-SUDA, 2024 launch), interplanetary and interstellar dust (IMAP-IDEX, 2024), the particles ejected from asteroids (DESTINY+, 2024) and comets (Comet Interceptor, 2029), the geysers of Enceladus, the aerosols of Titan, and the volcanoes of Io and Triton. While technology for obtaining mass spectra of solid particles is advancing, there has been less attention to analyzing the data to reach science objectives. Mission proposal reviews have picked out this lack as a weakness. For example, reviewers of the FOSSIL 2019 Discovery concept found "*The proposal did not convincingly demonstrate that it would be possible to identify mineral composition and phases from bulk chemistry for polyphasic particles, particles of mixed composition, and glass phases, all of which are important components of the interplanetary dust particle population.*" An impact-ionization dust instrument is now under discussion for inclusion on an Io volcanic plume sample return proposal JPL is developing for the New Frontiers program.

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Publications:

- *Detection of the Amino Acid Histidine and its Breakup Products in Hypervelocity Impact Ice Spectra.* Ulibarri, Munsat, Voss, Fontanese, Horanyi, Kempf, & Sternovsky, under review at Icarus.
- *Composition Measurement Capabilities of the Hyperdust Instrument From Laboratory Accelerator Experiments with Sub-Micron Particles of Crystalline Olivine.* Ayari, Hillier, Horanyi, Mikula, Munsat, Schmitt, Sternovsky, Trieloff, Turner, Ulibarri, & Westphal. Review of Scientific Instruments, in preparation.
- *Identifying Planetary Materials Through In Situ Impact-Ionization Mass Spectrometry.* Ayari, Horanyi, Munsat, & Turner. Planetary & Space Science, in preparation.
- *Impact Ionization Mass Spectra of Polypyrrole-Coated Anthracene Dust Particles.* Mikula & Sternovsky. Journal of Geophysical Research: Space Physics, in preparation.

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