Isotopic analysis of presolar dust grains with the NanoSIMS

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Although presolar grains isolated from primitive meteorites have been studied in detail for their isotopic compositions, most analyses have been limited to grains ≥1µm [e.g., 1, 2]. The NanoSIMS with its high sensitivity and high spatial resolution [3] makes it possible to analyze sub-micron grains, characteristic of the size of interstellar dust [4]. This capability has resulted in several isotopic studies of grains that previously would not have been possible.

One example is the analysis of presolar spinel grains from the Murray carbonaceous chondrite [5]. Oxygen isotopic measurements showed that the abundance of presolar grains ≤0.5µm is much higher (~2% of all spinel grains) than that of ≥1µm grains (~0.1%). Magnesium isotopic measurements of these presolar spinels revealed large 26Mg excesses [6]. Inferred initial 26Al/27Al ratios are much higher than expected from shell H burning in asymptotic giant branch (AGB) stars and require extra mixing (cool bottom processing).

Another example is the discovery of presolar silicates in interplanetary dust particles (IDPs) [7, 8] and in primitive meteorites [9, 10]. These grains are ≤1µm and although their abundances are higher than those of most other presolar grain types identified so far (~180ppm in a primitive meteorite and ~890ppm in IDPs), only the analysis of many thousands of grains by high-spatial-resolution isotopic imaging has made their identification among an overwhelming majority of isotopically normal silicate grains of solar-system origin possible.

References

O- and S-isotope imaging of primitive solar system materials with the Mainz NanoSIMS

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Introduction

Primitive meteorites and IDPs contain small quantities of nm- to µm-sized presolar grains that formed around evolved stars [1]. The invention of the NanoSIMS with its superior lateral resolution (<100 nm) and capability for the search of in-situ presolar dust in slices of IDPs [2] and meteorites [3] has opened a new window in this field of astrophysical research. Here, we will present results from NanoSIMS imaging surveys of O- and S-isotopic compositions in the Acfer 094 and Bishunpur meteorites and in two IDPs.

Acfer 094 and Bishunpur

O-isotope mapping with lateral resolution of 100 nm was performed on the matrix in polished thin sections of Acfer 094 and Bishunpur. Based on large O-isotopic anomalies we identified 17 presolar silicate and 3 presolar spinel grains, 150 to 600 nm in size. The O-isotopic compositions (and Si- and Fe-isotopic compositions, measured on a subset of those grains) point to origins from RGB and AGB stars. Matrix-normalized abundances are estimated to be 15 ppm (Bishunpur) and 130 ppm (Acfer 094) for silicates and 50 ppm for spinel (Acfer 094).

S-isotope mapping was done on selected areas of the matrix in Acfer 094. Automatic particle recognition revealed some 400 S-rich grains, two of which exhibit large negative 34S/32S anomalies of ~3σ. Whether these anomalies are just statistical outliers or the signature of real presolar matter remains to be seen.

IDPs U2071J2 and U2071C9

O-isotopic mapping was performed on four microtome sections of IDP U2071J2 (9×5 µm²) and on seven microtome sections of IDP U2071C9 (12×8 µm²). No presolar grains were found. Upper limits for presolar grains in these two IDPs of several 100 ppm are inferred.

References
Distinguishing solar and extrasolar origins of submicrometer grains in IDPs

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Interplanetary dust particles (IDPs) are primitive solar system objects from comets and asteroids that contain abundant interstellar materials [1]. These materials include D- and 15N-rich organic matter formed in a cold molecular cloud environment and grains of stardust [2]. The presolar (stardust) grains are identified by their exotic isotopic compositions that significantly differ from solar isotopic compositions [3]. Silicates are the most abundant type of stardust, but because of their small size (< 1 μm) were only recently discovered. The Cameca NanoSIMS ion microprobe was key to this discovery. The NanoSIMS uses an ultra fine beam of (50 nm) Cs+ and detects five mass lines simultaneously in imaging mode with high transmission at high mass resolving power. In practice, presolar grains as small as 200 nm can be measured in situ from solar system materials.

Silicates are more abundant in IDPs (450 – 5,500 ppm) than in meteorites (< 130 ppm), possibly because they are from comets [3,4]. A key issue to be resolved is the true proportion of presolar grains and solar system materials. Much of the material in IDPs is too fine grained (< 200 nm) to distinguish between solar and extrasolar origin. Some presolar silicates are amorphous (GEMS; 5), and may be mixtures of stardust and deposited material. The problem is further compounded by recent compositional mapping of GEMS grains by field emission TEM, showing that many GEMS grains are composite objects [6]. The isotopic measurement of GEMS grains may thus represent an average of still smaller subgrains. Resolving this issue may require higher precision isotopic measurements as the NanoSIMS is near the limiting size scale accessible to SIMS.

References


NanoSIMS Mg isotope analyses of refractory inclusions in metal-rich CB chondrites

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Hammadah al Hamra (HH) 237 is a metal-rich (CB) chondrite with unusual mineralogical and chemical signatures. HH237 appears to be a remarkably pristine relic of large-scale high temperature processes in the very early solar nebula [1]. We present Mg isotope analyses of refractory inclusions in HH237, collected with the LLNL NanoSIMS, demonstrating large mass-dependent isotope fractionation and excesses of radiogenic 26Mg.

Mg isotope compositions were measured by static multicolletion at a mass resolving power of ~4000, using a 20 pA, 250 nm 18O primary ion beam rastered over a 4x4 mm area. Isotope ratios were calculated using the sample-standard bracketing approach [2]. Ca-Al-rich inclusion (CAI) HH237-s #1 is a compact CAI composed of grossite (CaAl₂O₄) surrounded by a melilite-pyroxene rim with enclosed metal blebs; HH237-MW #4 is a fine-grained, hibonite-rich CAI containing minor spinel, melilite and perovskite, surrounded by layers of melilite and Al-diopside; HH237-104 CA1#1 is a spinel-ribonite spherule containing hibonite laths surrounded by a spinel mantle and a melilite-pyroxene rim. NanoSIMS analyses show large mass-dependent fractionation in all three CAIs favoring the lighter Mg isotopes with F(26Mg/25Mg) values ranging from -20 to -12 ‰/amu; 2σ is ~4‰/amu. Both hibonite-rich CAls exhibit large 26Mg excesses, with initial 26Al/27Al ratios of (7.5±3.3) x 10⁻⁵, while the grossite-rich inclusion contains no excess 26Mg with 26Al/27Al<2x10⁻⁶.

The large enrichment of the lighter Mg isotopes is unusual for igneous CAIs and, together with group II REE patterns [1], indicate many CAIs in CB meteorites preserve primary condensation signatures inherited from the nebular gas. The isotope fractionation effects appear decoupled from incorporation of 26Al. Additional refinement of initial 26Al abundances will elucidate the time scales of condensation and melting and test the hypothesis grossite-rich CAIs formed before injection of 26Al into the solar nebula.

References

Microscale D/H and C/H imaging of meteorites and IDPs – Calibration of ion microprobe data with terrestrial analogues and meteoritic residues

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Chondrites and interplanetary dust particles (IDPs) show large C contents and inhomogeneously distributed, strongly elevated D/H ratios compared to Earth and the solar system. The anomalies are mainly carried by organic matter that was formed in the interstellar medium and subsequently altered by parent body processing (Alexander et al., 1998). The carriers of the isotope anomalies have not unequivocally been identified, but µm-scale isotopic and elemental imaging by ion microprobe provides useful information. For example, quantitative D/H, C/H and 15N/14N imaging has been used to identify at least three distinct types of carbonaceous material in IDPs (Aléon et al., 2001, 2003). In general, the highest D/H ratios are associated with C, but high D/H ratios have also been observed in some C-poor regions of IDPs (Mukhopadhyay and Nittler, 2003). Precise C/H ratios are hence essential to distinguish the phases and ultimately identify the carriers of the various D/H signatures in IDPs. However, element ratios are difficult to determine with ion microprobes due to matrix effects depending on secondary yields.

We have begun a systematic examination of the isotope and element fractionation of our Cameca 6f imaging system (Nittler and Messenger, 1998). Various well-characterized extraterrestrial and terrestrial organic samples with a large range of C/H and D/H ratios such as coals, aromatic and aliphatic hydrocarbons, hydrated minerals and organic residues of primitive meteorites will allow us to precisely establish calibration ratios for C/H and D/H, to assess possible matrix effects and to determine realistic uncertainties. Furthermore, imaging data for µm-sized matrix particles from a range of meteorite types will be presented in order to enlarge the database for both weathered and relatively unaltered primitive chondrites allowing for a comparison with IDPs and returned STARDUST samples.

References

TOF-SIMS – A tool for sub-micrometer analysis in geo- and cosmochemistry

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Introduction

The analysis of micrometer and even sub-micrometer-sized samples has become more and more important in geo- and cosmochemistry. Typical examples are individual interplanetary dust particles (IDPs), ~10 µm in size, that often consist of hundreds of smaller grains. Some of these phases are isotopically highly anomalous, presolar grains embedded in isotopically normal, solar matter. These grains provide us with information about stellar and interstellar processes that formed the building blocks of our solar system.

TOF-SIMS

Time-of-flight secondary ion mass spectrometry (TOF-SIMS) is one of the techniques that are ideally suited for these tiny, complex samples (Stephan, 2001). With TOF-SIMS major, minor, and trace elements, their isotopes, and molecules can be measured at a lateral resolution of ~200 nm.

The main advantage of TOF-SIMS compared to double-focusing ion microprobes is its detection of all secondary ions with one, selectable polarity in a single experiment. This is due to the time-of-flight principle where even the heaviest molecular ion eventually reaches the detector. Therefore, hydrogen, e.g., can be measured simultaneously not only with all elements that form ions with the respective polarity but also with the heaviest bio-molecules. Further major differences to other SIMS instruments are little sample consumption (typically only a few atomic monolayers are sputtered during a measurement) and high transmission (20–80 %, depending on the ion species). However, count rates for individual ion species are rather low and statistical errors are often limiting the measurement accuracy, especially for isotope analysis.

Conclusion

Whenever high lateral resolution is required, and pre-selection of ion species to be measured has to be avoided, especially for samples with unknown composition, TOF-SIMS is an extremely valuable tool that can provide a huge range of information with a minimum of sample destruction.

Reference
**Hyperspectral data analysis of martian meteorite alteration: A tool for constraining surface processes on Mars?**

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**Introduction**

Our information-base regarding in situ analysis of surface materials stems from a handful of spacecraft missions. Large areas of Mars are apparently coated with a layer of surface fines (dust) that are quite similar in composition, suggesting this material has been distributed globally. Knowledge of aqueous processes beneath the surface of Mars is severely restricted, however, preterrestrially altered portions of the Martian meteorites offer an opportunity to directly examine low temperature precipitates. Some have pointed-out the similarities between the major element chemistry of micrometer scale alteration products and Martian dust [1]. In this study, we have analyzed Time-of-Flight Secondary Ion Mass Spectrometry (ToF-SIMS) data using multivariate statistical analysis (MVA) to compute the “local bulk composition” of secondary mineral veinlets to rigorously evaluate a chemical linkage to Martian dust. In doing so, we can also evaluate the possibility that Martian dust was processed aqueously.

**Approach and Results**

Because the kinetics of low temperature reactions in the Martian crust are slow, the products have small grain sizes (µm to sub µm), or are finely zoned amorphous phases [2]. As a result, ToF-SIMS and a pulsed Ga⁺ ion beam (~300 nm) were used to characterize these delicate secondary mineral assemblages. One advantage of ToF-SIMS is that all secondary ions are collected (effectively in parallel) at each pixel, producing a 3D hyperspectral data cube. We have processed several such mass-resolved data cubes using MVA (e.g. multivariate curve resolution) to compute the major, minor, and trace element compositions of “bulk” alteration. Our initial findings, based upon Si/Fe for example, suggest that aqueously altered silicates in meteorite alteration are distinct from soils analyzed by MER rover instrumentation. These findings suggest that Martian dust likely formed by a process distinct from low-T aqueous alteration.

**References**


**Carbonate-silicate assemblages in the Lafayette martian meteorite**

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**Introduction**

Some secondary mineral assemblages in Martian meteorites have long been interpreted as preterrestrial [1]. Poorly crystalline clay veinlets within nakhlitic olivines [1,2] and carbonate veinlets in Lafayette olivine [3-5] are probably the result of aqueous alteration in a near surface setting within the last 700 Ma [6]. Carbonate veinlets contain central silicates, zoned from the center outward, in the following way: amorphous Si-rich phase, amorphous Fe-rich phase, followed by poorly crystalline clays. Two microanalytical tools including full-spectrum X-ray mapping and time-of-flight secondary ion mass spectrometry (ToF-SIMS) were used to reveal the distribution of major, minor, and trace elements within these assemblages. ToF-SIMS has the unique capability of detecting a large suite of trace elements (e.g. Li, Be, B, Sc, V, Cr, Co, Ni, Cu, Rb, Sr, and Ba) in parallel on the sub micrometer scale, allowing one to evaluate different depositional models.

**Results**

We examined five different carbonate-silicate assemblages in Nakhl olivine. The minor and trace element composition of different silicate phases is complex.

Poorly crystalline clays: Most element abundances differ only within a factor of two, suggesting clays are similar in all carbonate veinlets. However, Be, Ti, Cr, Cu, and Ba show distinctively greater variability. Fe-rich amorphous material: Compositional variation is more restricted relative to clays, including Ti abundances. Si-rich amorphous material: This phase exhibits the greatest variability between veinlets.

These findings are best explained by low and decreasing water/rock ratios during veinlet formation. Thus, the local mineralogy (100s of µm) seemingly was increasingly important in determining veinlet fluid chemistry.

**References**

Microbial C and N assimilation in soils and model systems as revealed by ToF-SIMS

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Our research has utilized sub-µm ion probes in conjunction with time of flight secondary ion mass spectrometry (ToF-SIMS) for studying C and N assimilation in soil microbes. Early proof of concept studies using $^{13}$C and $^{15}$N labelled substrates clearly showed that C and N assimilation are detectable in single microbes using secondary ions of CN$^{-}$ isotopes. Because of practical limitations, high spatial resolution analyses are typically performed at low mass resolution. We were able to use a simple subtraction algorithm to remove $^{12}$C$^{14}$N$^{-}$ form the total $^{12}$CN$^{-}$ peak and quantify organic $^{15}$N isotope ratios. We applied this algorithm to region of interest analyses of microbes adhering to Si contact slides from soils and model soil systems. These studies have shown that microsite heterogeneities consisting of concurrent assimilation of inorganic N and rapidly mineralizing-organic-N may exist separated by only tens to hundreds of microns.

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Applications of SIMS Microanalysis at NIST

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Three Secondary Ion Mass Spectrometry (SIMS) instruments have been used for various microanalytical measurements applied to, or have the potential to be applied to geochemically interesting problems. Two of the instruments are dynamic SIMS magnetic sector instruments, a Cameca ims-4f and an ims-1270, and one is an IonTof Tof-SIMS IV. In addition to the measurement of sub-micron particles and structures, various cluster primary ion beams have been explored to enhance signals from organic materials as well as to limit damage of sub-surface layers to enhance our ability to obtain ultra-shallow depth profiles and depth profiles of organic materials.

Applications and measurements made with each of the instruments at NIST will be shown and discussed. Measurements of depth profiles, trace element abundances will be addressed, as well as isotopic ratios of natural minerals and anthropogenic materials. The importance of these measurements not only to geochemistry but to industry and international matters will be touched upon. Comparisons and limitations of each of the instruments will be addressed, specifically with respect to spacial resolution, both laterally and as a function of depth. Implications of signal intensity for hyperspectral analysis from limitations of secondary ionization, increased lateral resolution, and depth resolution will also be discussed.