NanoSIMS and more: New tools in nuclear astrophysics

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Abstract. Primitive Solar System materials contain nm- to μm-sized presolar grains that formed in the winds of evolved stars and in the ejecta of stellar explosions. These samples of stardust can be analysed in terrestrial laboratories with sophisticated analytical instrumentation in great detail. Of particular importance are coordinated studies of individual grains by Secondary Ion Mass Spectrometry (SIMS), Resonance Ionization Mass Spectrometry (RIMS) and Focused Ion Beam/Transmission Electron Microscopy (FIB/TEM) from which detailed information on isotopic compositions and mineralogies can be obtained. A key tool is the NanoSIMS 50 ion probe which permits to do isotope measurements of light and many intermediate-mass elements with spatial resolutions of <100 nm. A new type of RIMS instrument, “CHILI”, is currently under construction and is aimed to provide <100 nm resolution for isotope studies of intermediate-mass and heavy elements. Another promising analysis technique for future studies is Atom Probe Tomography (APT) which might be useful to create 3D-elemental and isotopic maps of presolar grains at the nanometer scale.

1. Introduction
Isotope studies are important tools in cosmochemical research to obtain detailed information on chemical and physical processes involved in the formation and alteration of extraterrestrial materials. One type of extraterrestrial material which is of high relevance for nuclear astrophysics are the so-called presolar grains [1, 2]. Presolar grains are nanometer to micrometer in size and are found in small quantities (up to several 100 ppm) in primitive meteorites, interplanetary dust particles (IDPs), and cometary matter. They are older than our Solar System and formed in the winds of evolved stars and in the ejecta of stellar explosions. Presolar grains exhibit large isotopic anomalies, the nucleosynthetic fingerprints of their parent stars. Among the identified presolar grains are diamonds, graphite, silicon carbide (SiC), silicon nitride (Si₃N₄), refractory oxides, mostly corundum and other forms of Al₂O₃ and spinel (MgAl₂O₄), and various silicates. These samples of stardust can be analyzed in the laboratory with sophisticated analytical instrumentation in great detail. Figure 1 illustrates the transport of presolar grains from their stellar sources to terrestrial laboratories.

Of particular importance are coordinated studies of individual grains involving Secondary Ion Mass Spectrometry (SIMS), Resonance Ionization Mass Spectrometry (RIMS), and Focused Ion Beam/Transmission Electron Microscopy (FIB/TEM). Such studies have provided a wealth of astrophysical information, not only on stellar nucleosynthesis and evolution, but also on Galactic chemical evolution, dust formation in stellar environments, chemical and physical processes in the interstellar medium, the types of stars that contributed dust to our Solar System, and on processes in the early Solar System.
Figure 1. Path of presolar grains from their stellar sources to terrestrial laboratories. After formation in the winds of evolved stars or in the ejecta of stellar explosions (1) and passage through the interstellar medium they became part of the molecular cloud from which our Solar System formed (2). They survived the early history of Solar System formation inside small planetary bodies (3) and are carried to the Earth by meteorites and IDPs (4). Finally they can be studied in detail for isotopic compositions and physical properties in the laboratory (5). Picture credits: NASA/JPL-Caltech (2), NASA/JPL (3), J. Koblitz (4), NASA/JPL-Caltech/STScI/Cxc/SAO (background).

FIB/TEM provides detailed information on the mineralogy and physical properties of individual presolar grains [3, 4]. The latest generation SIMS instrument, the NanoSIMS 50 ion probe, permits to do isotope measurements of the light and intermediate mass elements at the <100 nm scale, making it a powerful tool to study a large number of isotope systems in presolar grains [5]. By NanoSIMS ion imaging it is possible to create isotope maps which can be used (i) to search for presolar grains with specific isotopic fingerprints, e.g., the rare SiC supernova (SN) grains (figure 2), among chemical grain separates and (ii) to identify presolar grains in-situ in thin or FIB sections of meteorites and IDPs. RIMS has been used to measure the isotopic compositions of the heavy elements in presolar grains at the micrometer scale. A new type of RIMS instrument, “CHILI”, is currently under construction and is aimed to provide <100 nm resolution and better sensitivity [6]. Another promising analysis technique for future studies is Atom Probe Tomography (APT) which might be useful to create 3D-elemental (and possibly isotopic) maps of presolar grains at the nanometer scale [7].

Figure 2. Carbon- and N-isotopic systematics of presolar SiC grains. The vast majority (>90%) of the grains originate from AGB stars. Grains from SNe are the type C and X grains which make up about 1-2 % of all SiC grains. The solar C- and N-isotopic ratios are indicated by the dashed lines. From [8].

In the following I will briefly describe technical aspects of the NanoSIMS (chapter 2), of RIMS (chapter 3), and of APT (chapter 4) as well as their applications in presolar grain research.
2. The NanoSIMS ion probe

In SIMS a solid surface is bombarded by a finely focused primary ion beam. This triggers a collision cascade in the target which causes atoms and small molecules from the upper layers of the sample to be ejected. A small fraction (up to the percent range) of these sputtered particles is ionized and can be analyzed in a mass spectrometer. For a detailed description of the SIMS technique see, e.g., [9].

The Cameca NanoSIMS 50 ion probe is a double-focusing, magnetic sector, multi-collecting SIMS instrument [10, 11]. Primary ions are either oxygen (O\textsuperscript{-}) or cesium (Cs\textsuperscript{+}). O\textsuperscript{-} primary ions favor formation of positive secondary ions (e.g., alkali, alkaline earth, and transition metals) and Cs\textsuperscript{+} formation of negative secondary ions (e.g., C, O, CN, Si, S). The ion optics of the NanoSIMS was specifically designed for high spatial resolution (i.e., small primary beam diameter) and high transmission for secondary ions; for a schematic of the ion optics see figure 3. A mass resolution of several 1000 is easily achieved which permits to do isotope measurements of the light and of many intermediate-mass elements.

The NanoSIMS is characterized by four fundamental features, which makes it an extremely useful tool to study presolar grains: (i) High spatial resolution of down to 50 nm for Cs\textsuperscript{+} primary ions and down to 200 nm for O\textsuperscript{-} primary ions. (ii) High useful yields (= detected ions/sputtered atoms) up to the percent level for certain elements. (iii) Simultaneous detection of up to 7 isotopes (depending on the configuration of the instrument). (iv) Ion imaging capabilities (see below).

Figure 3. Schematic of the ion optics of the NanoSIMS 50. Picture credit: François Hillion and Frank Stadermann.

Ion imaging is a key feature of the NanoSIMS. Ion images can be acquired by rastering the focused primary ion beam over a region of interest. Samples are typically individual grains dispersed on clean substrates (e.g., Au foils) or meteoritic thin and FIB sections. Specific procedures were developed for
grain samples that permit to measure isotopic compositions of a large number of individual grains in a fully automated way in relatively short time [12, 13]. These procedures were used to measure C- and Si- or O-isotopic compositions with Cs$^+$ primary ions and consist basically of three steps: (i) Ion images of selected isotopes are recorded with a spatial resolution of ~100 nm for a square region with typical side length of 20-30 $\mu$m (figure 4). (ii) Individual grains are identified by grain recognition routines in one of the ion images. (iii) Individual grains are measured with much higher precision than in step (i) in that only small areas with ~2 times the grain size around each identified grain are measured. (iii) Movement of the sample stage to an adjacent area and repetition of steps i to iii. Application of this technique has been particularly useful for the search of rare presolar grain types, e.g., the SiC SN C grains, which exhibit strong enrichments in the heavy Si isotopes [14-16], or oxide grains with extreme O-isotopic compositions [13].

Figure 4. Left: $^{28}\text{Si}$ ion image (30 x 30 $\mu$m$^2$) of presolar SiC grains from the Murchison CM2 meteorite dispersed on a Au foil. The grain inside the green circle is a submicrometer-sized SN X grain, as indicated by its Si-isotopic signature. Right: Scanning electron microscopy (SEM) image of the same area; several NanoSIMS measurement fields of individual grains (cf. step ii in automated ion imaging) are clearly visible in this picture.

The identification of these rare grains provided new insights into nucleosynthesis and dust formation in explosive environments. One of the oxide grains has massive enrichments in $^{17}\text{O}$, $^{25}\text{Mg}$, and $^{26}\text{Mg}$, which are isotopic signatures indicative of condensation from nova ejecta [13] (figure 5). Another extremely $^{16}\text{O}$-rich grain shows clear evidence for extinct $^{44}\text{Ti}$, which can be considered as proof for the SN origin of $^{16}\text{O}$-rich grains [13] (figure 5). For SiC C grains follow-up measurements showed that many of them have isotopically light S (i.e., $^{32}\text{S}$ enrichments). This is hard to understand in the context of current Type II SN (SNIa) models [17] as Si- and S-isotopic signatures (i.e., light, heavy, or solar) follow each other in the different zones. Hoppe et al. [15] invoked preferential incorporation of S from the Si/S zone (which has light S) over S from other zones resulting from molecule chemistry in still unmixed SN ejecta to account for this observation. More recently, Pignatari et al. [18] presented an alternative explanation, namely, decay of radioactive $^{32}\text{Si}$ (half life 153 yr). This nuclide is predicted to be produced by explosive He burning in SNeII in large amounts which, if incorporated by the growing SiC grains and after decay, could fully account for the observed $^{32}\text{S}$ enrichments in C grains.
Figure 5. Oxygen-isotopic compositions of different populations of presolar silicate and oxide grains. The solar O-isotopic ratios are indicated by the dashed lines. The $^{16}\text{O}$-rich SN grain with evidence for extinct $^{44}\text{Ti}$ and the grain with extreme $^{17}\text{O}$ enrichment (possibly a nova grain) were identified by automated ion imaging in the NanoSIMS [13]. From [8].

Figure 6. $^{17}\text{O}/^{16}\text{O}$ ion image of a 5 x 5 $\mu$m$^2$-sized area in the matrix of the Acfer 094 meteorite. This image was acquired with a 50 nm-sized primary Cs$^+$ ion beam. A presolar silicate grain (490 x 250 nm$^2$) with an $^{17}\text{O}$ enrichment of a factor of ~3 stands out as bright hotspot. From [19].

Ion imaging of meteoritic thin or FIB sections has been particularly important to identify presolar silicates which have typical sizes of 200-400 nm and which, contrary to refractory presolar oxides and carbonaceous presolar material, can not be separated by chemical treatments from meteorites. They were identified by O ion imaging with the NanoSIMS, first in an IDP [20] and later also in meteorites [21, 22]. Presolar silicates were also identified with a SCAPS detector on a Cameca IMS 1270 ion probe [23]; however, this technique reliably identifies only the largest (>500 nm) presolar grains. NanoSIMS O ion imaging of meteoritic thin and FIB sections is now a well-established technique and hundreds of presolar silicates (along with some presolar oxides which have lower abundances) have been found in the matrix of primitive meteorites and in IDPs (figure 6). Apart from getting information on nucleosynthetic processes in and evolution of their parent stars, observed abundance variations among different primitive Solar System materials provide information on thermal and aqueous alteration on their parent bodies and on possible abundance variations in the Solar nebula [24, 25]. Isotope data other than for O are rare for presolar silicates. This is because the Si$^+$ ion yield is relatively low in O-rich environments, resulting in comparatively large (compared to SiC) uncertainties for Si-isotopic ratios. Other major elements of silicates, e.g., Mg and Fe, must be measured with the O primary ion source. Here, the size of the primary ion beam is of comparable size to that of presolar silicates and measured isotope ratios strongly suffer from dilution effects with surrounding solar material. FIB sample preparation techniques have been developed to minimize dilution effects and Mg isotope data were obtained for some grains [26, 27].

3. Resonance Ionization Mass Spectrometry
A fundamental difference between SIMS and RIMS is that RIMS uses the usually >99% of neutral particles released by ion sputtering or laser desorption for mass spectrometric analysis. RIMS can be used to measure the isotopic compositions of most elements in the periodic table; several of the major
and minor elements in presolar grains, e.g., C, N, O, and S, however, are not accessible by RIMS. Most of the measurements on presolar grains made by RIMS so far were done with an instrument named CHARISMA (Chicago-Argonne Resonant Ionization Spectrometer for Mass Analysis). In this instrument material from a grain is desorbed by a pulsed laser (Nd-YAG) beam, the element of interest is resonantly ionized with tunable Ti:sapphire lasers, and ions are finally analyzed by time-of-flight (TOF) mass spectrometry [28]. Useful yields of CHARISMA are in the percent range and useful and important results were obtained for the isotopic compositions of intermediate-mass and heavy trace elements, e.g., Sr, Zr, Mo, Ru, and Ba in individual, micrometer-sized presolar grains [29-33].

Currently, a new type of RIMS instrument, “CHILI” (Chicago Instrument for Laser Ionization), is under construction at the University of Chicago [6] (figure 7). This instrument employs a finely focused Ga ion beam with nominal beam diameter of 2.5 nm for sputtering. The sputtered, neutral particles are resonantly ionized by six tunable Ti:sapphire lasers. CHILI is aimed at measuring isotopic compositions of intermediate-mass and heavy elements at sub-micrometer resolution, possibly even with better than 50 nm. Useful yields are much higher than for CHARISMA, reaching values of 40%. This is particularly important as CHILI is intended to carry isotope measurements to much smaller scales than is possible with CHARISMA. CHILI will not only allow to expand isotope measurements to additional trace elements and to access smaller grains but at <50 nm scales even subgrains within presolar grains become accessible for isotope studies. Altogether this has great potential to get new insights into nucleosynthetic processes and dust formation in stellar environments.

Figure 7. Principle of CHILI. A liquid Ga ion gun is used for sputtering. Photo ions are produced by resonance ionization with tunable Ti:sapphire lasers and analyzed with a time-of-flight mass spectrometer. An electron gun is available to produce secondary electron images of the sample. Picture credit: Thomas Stephan.

4. Atom Probe Tomography
Atom probe tomography is an established technique in the materials science [34]. In recent years, attempts have been made to apply APT to the study of presolar grains [7]. APT uses so-called field evaporation and offers chemical and isotopic analyses with sub-nm spatial resolution. Of particular importance is the preparation of the sample which must be shaped to a very sharp tip (figure 8, left). A high voltage is applied to the sample which results in a very strong electrostatic field close to the tip. Atom removal is triggered by a laser pulse and ionization occurs due to the strong electrostatic field. Ionization is close to 100 % and ions are mass-analyzed (time-of-flight) and monitored with a position-sensitive detector. Repeated application of the laser pulse permits to create 3-dimensional chemical and isotopic maps at the nm- or even sub-nm scale.

A potential application of APT of high interest in presolar grain research are measurements of C-isotopic ratios of individual meteoritic diamonds. Meteoritic diamonds are only 2-3 nm in size, i.e., individual grains are not accessible by currently used isotope measurement techniques. Bulk diamond samples exhibit isotope anomalies in the trace elements Xe and Te [35, 36], indicative of a presolar origin. But because bulk C- and N-isotopic ratios of meteoritic diamonds are essentially solar [37], it is not clear which fraction of them is true stardust. Attempts to measure C-isotopic ratios in individual diamonds by ATP are currently ongoing [7] (figure 8) and it will be interesting to see whether reliable and useful results can be obtained. If successful, use of APT could open new and interesting applications in presolar grain research.
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