ELSEVIER

New Astronomy Reviews xx (2003), pp

New Astronomy Reviews
www.elsevier.nl/locate/newar

Developments in Instrumentation for Isotopic Analyses of Pre-Solar Grains

U. Ott, P. Hoppe and G.W. Lugmair

Max-Planck-Institut für Chemie (Otto-Hahn-Institut), Becherweg 27, D-55128 Mainz, Germany (ott@mpch-mainz.mpg.de)

Abstract

The bulk of the pre-solar grains that have survived in primitive meteorites are submicron in size. Isotopic analysis of single grains requires highly sensitive mass spectrometric methods. An important role in future investigations will be played by the NanoSIMS, which is also characterized by high spatial resolution. Complementary methods are coming into operation (RIMS) or are being improved (noble gas mass spectrometry) up to the point where almost all atoms of a given trace element will be detected.

Keywords: meteorites, presolar grains, isotope abundance anomalies; mass spectrometry; RIMS; SIMS; noble gases
PACS: 96.50.Mt, 26.45.+h, 07.75.+h,26.30.+k

1. Introduction

Following the discovery in primitive meteorites of isotope abundance anomalies in noble gases (Reynolds and Turner, 1964; Black and Pepin, 1969), and the realization that these were preserved stellar nucleosynthesis products carried by surviving pre-solar grains (Lewis et al., 1987; Tang and Anders, 1988a), the study of these grains has become a focus of meteorite research. It has also helped in building a bridge between meteoritics and astrophysics. Detailed analyses of single grains have shown that each carries its own individual isotopic signature inherited from its stellar source (Zinner, 1998; Hoppe and Zinner, 2000).

However, most grains are submicron in size (Amari et al., 1994; Zinner, 1998), and so far most individual grain analyses have been performed on relatively large grains, which may not be representative in all aspects. Analysis of the smallest grains requires highly sensitive mass spectrometric methods, and, depending on the specific type of question, may also require high spatial resolution. An important step forward is the introduction of a new generation ion microprobe, the NanoSIMS 50 (Hillion et al., 1993). Below we describe some of the important features and applications of the NanoSIMS. We also discuss progress in complementary methods more suited for specific elements or specific types of investigation: TOF-SIMS, RIMS, AMS, and noble gas mass spectrometry.

2. The NanoSIMS 50

2.1. *NanoSIMS features*

The NanoSIMS 50 ion microprobe is a new generation SIMS instrument. It is unique in that it combines high sensitivity with a high lateral resolution of ~50 nm when operated with the Cs^+ primary beam (~150 nm with the O^- primary beam). This is achieved by a design in which the primary beam hits the sample at 90° angle and the primary and extraction optics are co-axial (Fig. 1).

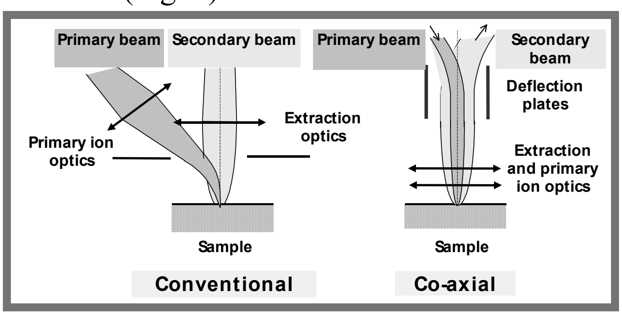

Fig. 1. Ion optics of the NanoSIMS 50 (right) in comparison with the conventional design (left).

Compared to our "old" SIMS, a Cameca IMS 3f, the transmission of the new instrument for secondary ions is a factor ~20-30 better for typical measurement conditions; it still remains several tens of % up to a mass resolution of 8000 (Fig. 2). In addition, the NanoSIMS has six detectors, where four are moveable, for simultaneous ion collection, resulting in a corresponding increase in effective detection efficiency. These detectors cover a mass range of a factor of ~16, so that elements widely differing in mass can be analyzed in the same run.

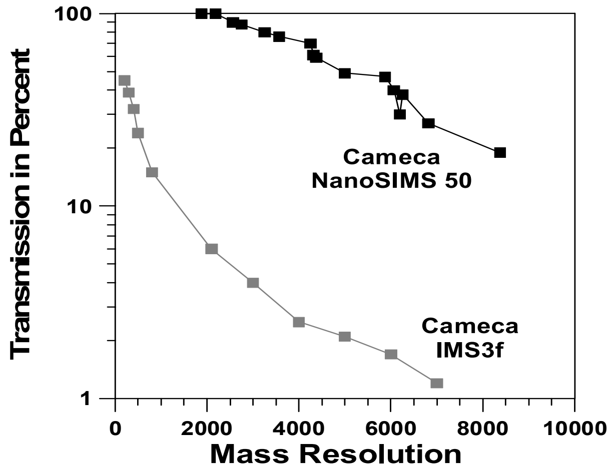

Fig. 2. Transmission of the NanoSIM50 as a function of mass resolution, in comparison with the IMS 3f ion microprobe.

2.2. *NanoSIMS 50 results / projects*

An overview of results obtained during the first two years of operation at MPI for Chemistry, Mainz, is given in a companion paper (Hoppe et al., 2003, this volume). This includes studies of extinct ^{26}Al, ^{53}Mn and ^{60}Fe in minerals formed very early in solar system history, as well as studies on presolar silicon carbide: s-process Ba in mainstream SiC, and extinct ^{44}Ti and ^{49}V in presolar SiC grains of supernova origin.

Isotopic mapping as described there for determining the spatial distribution of excess ^{44}Ca (from ^{44}Ti decay) within the grains is also employed in another currently ongoing project: *in-situ* search for pre-solar oxide grains. The technique is demonstrated in Fig. 3. Most of the known presolar oxide grains have high $^{17}O/^{16}O$ and low $^{18}O/^{16}O$ relative to solar values (e.g., Hoppe and Zinner, 2000). Thus, using isotopic mapping candidate grains can be identified for subsequent precise measurement.

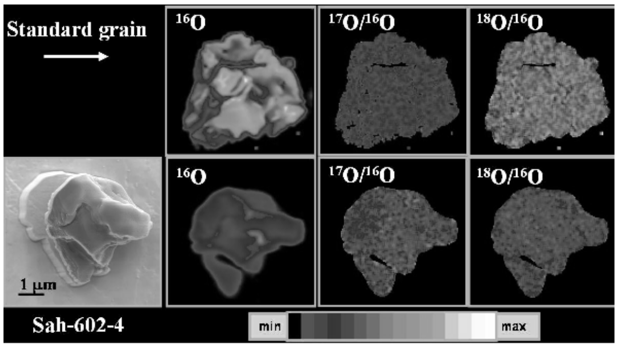

Fig. 3. Appearance of a typical pre-solar corundum grain in oxygen isotopic mapping (bottom). The grain Sah-602-4, shown as an example, was chemically isolated from the meteorite Sahara-97166 and shows high $^{17}O/^{16}O$ and low $^{18}O/^{16}O$ compared to the terrestrial standard grain (top). With the high lateral resolution of the NanoSIMS, this technique can be used for *in-situ* search of pre-solar candidate grains. Figure adapted from Mostefaoui et al. (2002).

3. Complimentary methods

While the NanoSIMS will be the workhorse for isotopic studies of pre-solar grains in the foreseeable future, its results will need to be complemented in specific cases by other methods. Some of these methods and technical progress therein will be briefly described below.

3.1. *TOF-SIMS*

A recent overview of the TOF-SIMS method and its application in cosmochemistry has been given by Stephan (2001). Compared to conventional SIMS, TOF-SIMS has higher lateral resolution, though not as high as the

NanoSIMS. A major advantage (inherent in the TOF method) is that data over the whole mass range can be obtained. However, because the ions arrive at the detector in short pulses, only small ion beams are allowed. The method serves well to study surface features, abundances of elements and their distributions, but it cannot compete with the NanoSIMS when it comes to specific and precise isotope measurements.

3.2. Resonance ionization mass spectrometry (RIMS)

Resonant ionization is a mature field in principle and can be applied to almost all elements (e.g., Saloman, 1994). Key players in the field of cosmochemistry and pre-solar grains have been the group at Argonne and (for the noble gas Xe – see below) the group at the University of Manchester. The Argonne instrument, dubbed "CHARISMA" and first described by Ma et al. (1995), has been constantly upgraded since then (Savina et al., 2003a).

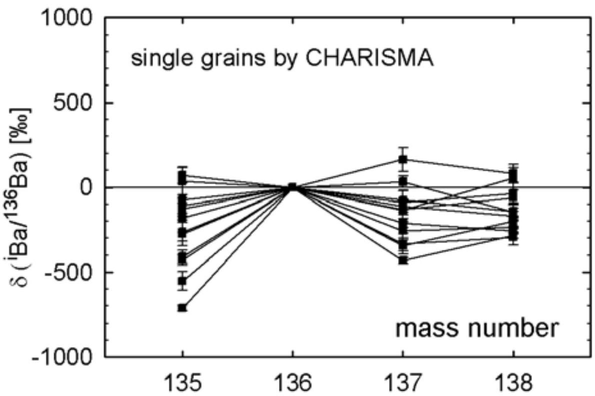

Fig. 4. Isotopic composition (relative to normal and ^{136}Ba) of Ba in individual presolar mainstream SiC grains. Data from Savina et al. (2003b). Errors are 1σ. Some results with large error (> 300 ‰ at ^{135}Ba) are not shown. No data have been reported for ^{134}Ba and the rare p-only isotopes ^{130,132}Ba.

As an example, results for Ba in single presolar SiC grains (Savina et al., 2003b) are shown in Fig. 4. The method has been also applied to the analysis of Zr, Mo, Sr and Fe in presolar graphite and/or SiC grains (see references in Savina et al., 2003a, b).

The method involves sputtering / desorption of atoms from a sample / grain using a pulsed laser beam, followed by laser ionization in the expanding cloud of atoms. Laser frequencies for the ionization step are chosen so that first a resonant state is reached (making the method element-selective), followed by the actual ionization in a second transition of different wavelength. Ions are extracted and measured by time-of flight mass spectrometry. For optimum efficiency, the atoms must be pumped from the intermediate resonant state to the ionization continuum much faster than they decay to lower-lying electronic states. The intermediate state must be efficiently populated by strongly saturating the resonance transition. CHARISMA, in its current configuration has an overall efficiency of ~ 1% (for Ba); i.e. ~ 1% of all atoms of the element of interest that are present in the sample are actually seen by the detector. Only for elements that are easily ionized and also not seriously compromised by isobaric interferences (molecular interferences can be resolved) the NanoSIMS is a more flexible alternative (cf. Hoppe et al., 2003; Marhas et al., 2003). Further upgrades are expected to bring the efficiency of CHARISMA to a remarkable 30% (Savina et al., 2003a).

3.3 Accelerator mass spectrometry (AMS)

Like RIMS, AMS is able to overcome the problem of isobaric interferences (and even more so). Since it is not as sensitive as RIMS can be, but has higher flexibility in switching between different elements, it is most usefully applied where sensitivity is not a major concern. An example is the case of trace elements in pre-solar nanodiamonds. On the average they consist only of ~ 1000 atoms but only a few contain a trace element atom of interest. So one has to measure many diamonds ("aggregates") anyway. First results by AMS have been reported for Pt (Merchel et al., 2003).

3.4 Noble gases

RIMS is also being applied in the study of noble gases, with stable isotope measurements performed (so far) of Xe only and only by the group at the University of Manchester. The instrument, named RELAX (first described by Gilmour et al., 1993), conceptually differs from CHARISMA in that the space where ionization takes place is separated from where the atoms are liberated. The reason is the low concentration of Xe in most natural materials that hardly will allow measuring Xe released in one laser shot, or even from a whole single pre-solar grain, for that matter. For example, in a typical (~ µm-sized) grain of pre-solar SiC there is on average only about one atom of s-process Xe. As a consequence, Xe (liberated by whatever means) is frozen to a cryogenic sample concentrator in the mass spectrometer source region. For the actual mass spectrometric analysis some fraction is released from the concentrator by a heating pulse from a laser. This is then followed by resonance ionization and time of flight mass spectrometry as in the case of CHARISMA. Xenon that has been desorbed but not ionized will return to the sample concentrator and will be available for analysis during following heating shots. Judging from the errors in the measurement of air calibrations (Fig. 8 in Gilmour et al., 1993), overall efficiency of RELAX at the time must have been at least 10%.

Quite generally and not just in the RIMS version, noble gas mass spectrometry, in particular of Xe, is one of the most sensitive mass spectrometric measurement techniques. The reason is that since the pioneering work of Reynolds (1956), noble gases are measured statically, i.e. valves to the pumps are closed when the extraction of the gases from the solid sample starts. As a consequence, at the end of an analysis even in a conventional mass spectrometer essentially all the atoms of xenon will have been ionized. Two principal approaches can be envisioned to improve performance, where both have been combined in the RELAX instrument: efficient registration of all ions that are ionized (inherent in time of flight mass spectrometry) and minimization of the volume in which the gas to be analyzed is contained (the concentrator in RELAX). Each of these independently or both combined can also be realized through modification of conventional instruments that use electron impact ionization in a magnetic mass spectrometer. In this way it may not be possible to reap all the benefits of RIMS /TOF mass spectrometry; nevertheless, it is possible to overcome some of its limitations: restricted application of RIMS (Xe and probably Kr only; with currently available lasers clearly not He and Ne with their large ionization potential), and the small dynamic range in TOF mass spectrometry.

Multiple detectors in a magnetic mass spectrometer will allow simultaneous collection of all isotopes of an element, thus in effect enhancing sensitivity compared to the conventional system by an order of magnitude (for Xe). Alternatively, the system can be used to collect the same number of ions in ~10x shorter time, thus decreasing uncertainties associated with memory effects and the need to extrapolate the measured composition to the time of gas inlet into the mass spectrometer. Such a detection system is currently under construction in our laboratory.

Higher ionization efficiency, thus shorter measuring time (for a given number of ions to be collected) and better signal/noise ratio can be achieved by increasing the partial pressure of the gases in the ion source. This approach is pioneered by the group at ETH Zürich, who have developed a compressor ion source, i.e. a combination of a sealed ion source and a molecular-drag pump. Sensitivity is increased by a factor of ~200 (Baur, 1999; Fig. 5). Since the partial pressure of background gases is also increased in the ion source, it is necessary to include a chemical getter in the ion source, however.

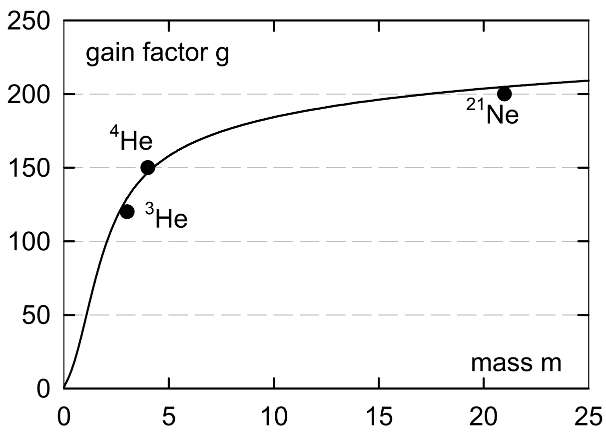

Fig. 5. Increase in sensitivity (gain factor) in the ETH compressor ion source as a function of mass; for a rotor speed chosen of 90,000 rpm. Information provided by H. Baur.

The system will probably be most useful in the study of He and Ne. It is less useful for heavy noble gases like Xe because their lifetime in the mass spectrometer would be decreased to something on the order of a minute. Using the system, it should be possible to extend the study of Ne-E (essentially pure ^{22}Ne) in pre-solar SiC and graphite to significantly smaller grain sizes as compared to previous work (Nichols et al., 1993, 1994, 2003). It may even allow searching for the even rarer spallogenic ^{21}Ne in single pre-solar SiC grains and thereby putting constraints on the pre-solar age of the grains (cf. Tang and Anders, 1988b). This will probably be feasible for the very largest grains only, because only there we may expect enough atoms of spallation Ne produced and not lost due to recoil (cf. Ott and Begemann, 2000). But it may help in finding an answer to one of the most principal questions concerning interstellar materials.

4. Conclusions

Measurements of isotopic compositions in pre-solar grains preserved in meteorites require highly sensitive mass spectrometric methods, if only for the small number of atoms of many elements. Study of isotopic distributions within the grains and/or *in-situ* search in the meteorites for preserved pre-solar grains requires also methods with high spatial resolution. The NanoSIMS 50 will be the tool of choice for many of the upcoming tasks. But for specific problems it will need to be complemented by other methods. Among these are RIMS for the study of trace elements and, for the specific case of noble gases, noble gas mass spectrometry. Significant progress is being made also in these fields, and in both effective detection efficiencies are likely to reach 10s of percent in the near future.

References

Amari, S., Lewis, R.S. and Anders, E., 1994, Geochim Cosmochim Acta 58, 459
Baur, H., 1999, EOS Trans AGU 80, F1118
Black, D.C. and Pepin R.,O., 1969, Earth Planet Sci Lett 6, 395
Gilmour, J.D., Lyon, I.C., Johnston, W.A. and Turner, G., 1993, Rev Sci Instrum 65, 617
Hillion, F., Daigne, B., Girard, F. and Slodzian, G., 1993, in: Secondary ion mass spectrometry SIMS IX (eds. A. Benninghoven, Y. Nihei, R. Shimizu, H.-W. Werner), 254. John Wiley & Sons Ltd.
Hoppe, P. and Zinner, E., 2000, J Geophys Res 105, 10371
Hoppe, P., Ott, U. and Lugmair, G.W., 2003, New Astr Rev, this volume
Lewis, R. S., Tang, M., Wacker, J. F., Anders, E. and Steel, E., 1987, Nature 326, 160
Ma, Z., Thompson, R.N., Lykke, K.R., Pellin, M.J. and Davis, A.M., 1995, Rev Sci Instrum 66, 3168
Marhas, K.K., Hoppe, P. and Ott, U., 2003, Meteorit Planet Sci 38, in press
Merchel, S., Ott, U., Herrmann, S., Spettel, B., Faestermann, T., Knie, K., Korschinek, G., Rugel, G. and Wallner, A., 2003, Geochim Cosmochim Acta, in press
Mostefaoui, S., Besmehn, A. and Hoppe, P., 2002, MAPS 37, A104
Nichols, R.H., Jr,., Amar,i S., Hohenberg, C M., Hoppe, P. and Lewis, R.S., 1993, Meteoritics 28, 410
Nichols, R.H., Jr., Kehm, K., Brazzle, R., Amari, S., Hohenberg, C.M. and Lewis R.S., 1994, Meteoritics 29, 510
Nichols, R.H., Jr., Kehm, K., Hohenbrg, C.M., Amari, S. and Lewis, R.S., 2003, Geochim Cosmochim Acta, submitted
Ott, U. and Begemann, F., 2000, Meteorit Planet Sci 35, 53
Reynolds, J.H., 1956, Rev Sci Instrum 27, 928
Reynolds, J.H. and Turner, G., 1964, J Geophys Res 69, 3263
Saloman, E.B., 1994, Spectrochim Acta 49B, 251
Savina, M.R., Pellin, M.J., Tripa, C.E., Veryokin, I.V., Calaway, W.F. and Davis, A.M., 2003a, Geochim Cosmochim Acta, in press
Savina, M.R., Davis, A.M., Tripa, C.E., Pellin, M.J., Clayton, R.N., Lewis, R.S., Amari, S., Gallino, R. and Lugaro, M., 2003b, Geochim Cosmochim Acta, in press
Stephan, T., 2001, Planet Space Sci 49, 859
Tang, M. and Anders, E., 1988a, Geochim Cosmochim Acta 52, 1235
Tang, M. and Anders, E, 1988b, ApJ 335, L31
Zinner, E., 1998, Annu Rev Earth Planet Sci 26, 147
Zinner, E., Amari, S. and Lewis, R.S., 1991, ApJ 382, L47