

NanoSIMS, the new tool of choice: ^{26}Al , ^{44}Ti , ^{49}V , ^{53}Mn , ^{60}Fe , and more

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Abstract

The NanoSIMS, a secondary ion mass spectrometer characterized by unique high transmission and high spatial resolution, is about to revolutionize the isotopic study of pre-solar grains and other rare minerals in meteorites. We discuss some of the results obtained using this instrument at the MPI for Chemistry, Mainz, during the first two years of operation on extinct ^{26}Al , ^{53}Mn and ^{60}Fe in meteoritic minerals as well as extinct ^{44}Ti and ^{49}V , and s-process Ba in pre-solar silicon carbide.

Keywords: meteorites, extinct radionuclides, presolar grains, isotope abundance anomalies, s-process

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1. Introduction

Since the first discovery and identification of preserved pre-solar grains in meteorites (Lewis et al., 1987; Bernatowicz et al., 1987), the study of their isotopic features has been one of the most active areas in meteorite research. Similarly, with excess ^{26}Mg from ^{26}Al first demonstrated by Lee et al. (1976), the study of the decay products of extinct radionuclides that were present in the early solar system has grown into a very active research area during the last decade. Pre-solar grains are typically nm to μm in size (e.g., Zinner, 1998). Hence, their study requires mass spectrometric measurement techniques with high sensitivity and, in addition, high spatial resolution, if searching for occurrences of pre-solar grains *in situ* or for the investigation of isotopic and elemental homogeneity within grains. The requirements are similar for the study of extinct radionuclides. In order to reliably establish their abundance level in the early solar system it is necessary to search for mineral phases with very high mother/daughter element ratio, which may enhance the potential for large isotopic effects. Thus, high sensitivity and (as demonstrated below) spatial resolution are essential as well.

As already outlined in the Proceedings of the previous Astronomy with Radioactivities Workshop (Hoppe, 2002), the new Cameca NanoSIMS 50 ion microprobe offers highly improved analytical capabilities in this field. This includes a lateral resolution (using the Cs^+ primary beam) of 50 nm (vs. $\sim 1 \mu\text{m}$ for traditional SIMS instruments) and high transmission ($\sim 30\times$ higher than the Cameca IMS 3f under typical operating conditions), which is clearly a major step forward (see also Ott et al., 2003). The first two instruments were installed in February and in May 2001 at the Washington University, St. Louis, and the MPI for Chemistry, Mainz. Here we describe some results obtained during the first ~ 2 years of operation at Mainz.

2. Radionuclides in the Early Solar System

The live presence of now extinct radionuclides in the Early Solar System was first established for the case of ^{26}Al by Lee et al. (1976), who demonstrated the existence of excesses in ^{26}Mg in Ca-Al-rich inclusions (CAIs) in meteorites that correlate with the Al/Mg elemental ratio. In the meantime a fair number of additional radionuclides have been found (Table 1), with half-lives ranging from possibly less than

two months (^7Be ; to be confirmed) up to ~ 100 Ma (^{146}Sm). Most attest to stellar nucleosynthesis contributions, probable exceptions being the Be isotopes (see also Goswami and Marhas, 2003). Of special interest in relation to early solar system history are ^{26}Al and ^{60}Fe , because they may have acted as heat sources for early melting of asteroidal bodies.

Table 1. Extinct radionuclides in the Early Solar System. As compiled in Ott and Lugmair (2002), except for an update for ^{60}Fe (Mostefaoui et al., 2003; Tachibana and Huss, 2003). In addition, evidence to be confirmed has been presented for the presence in CAIs of ^7Be ($T_{1/2} = 53$ d; Chaussidon et al., 2002).

nuclide	$T_{1/2}$	ref. nucl. ^a	\sim ratio
^{10}Be	1.5 Ma	^9Be	10^{-3}
^{26}Al	0.7 Ma	^{27}Al	5×10^{-5}
$^{36}\text{Cl}(?)^b$	0.3 Ma	^{35}Cl	1.4×10^{-6}
^{41}Ca	0.1 Ma	^{40}Ca	1.5×10^{-8}
^{53}Mn	3.7 Ma	^{55}Mn	$1-2 \times 10^{-5}$
^{60}Fe	1.5 Ma	^{56}Fe	1×10^{-6}
^{92}Nb	36 Ma	^{93}Nb	2×10^{-5}
^{107}Pd	6.5 Ma	^{108}Pd	2×10^{-5}
^{129}I	16 Ma	^{127}I	1×10^{-4}
^{146}Sm	103 Ma	^{144}Sm	7×10^{-3}
^{182}Hf	9 Ma	^{180}Hf	1×10^{-4}
^{244}Pu	81 Ma	^{238}U	7×10^{-3}

^a reference nuclide to which the abundance of the radionuclide (column 4) is normalized.

^b reported evidence probably due to experimental artifact (Rai et al., 2003).

2.1. ^{26}Al in ordinary chondrites

Most of the evidence for the presence of ^{26}Al in the early solar system comes from the study of Ca-Al-rich inclusions, many of which show the “canonical ratio” $^{26}\text{Al}/^{27}\text{Al} = 5 \times 10^{-5}$ (MacPherson et al., 1995). To ascertain whether ^{26}Al can be used as a fine-scale chronometer and whether it may have acted as a

heat source for melting small planetesimals requires that it was homogeneously distributed. A way to test this is measurement of the Al-Mg system in objects of different ages that have been reliably determined by other chronometers. To this end NanoSIMS measurements were performed on plagioclase grains in two different ordinary chondrites (Zinner et al., 2002).

The analyses were done on polished thin sections, in which the grains had previously been found by automatic EDX mapping. Hence, in contrast to earlier similar measurements (e.g., Zinner and Göpel, 1992), the petrographic context is well known. The size of the grains is rather large (Fig. 1), but the high spatial resolution of the NanoSIMS proved to be essential as it allowed avoiding during analysis the numerous tiny Mg-rich grains within the plagioclase.

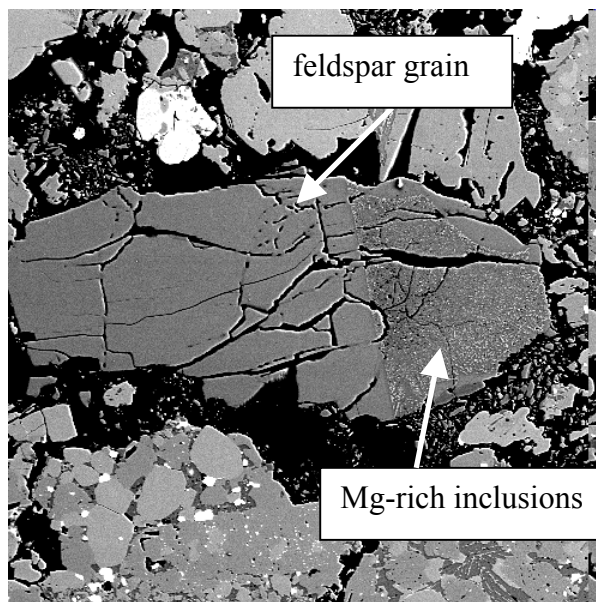


Fig. 1. Analyzed feldspar grain from Forest Vale (size ~ 300 μm). The part on the right contains numerous small Mg-rich inclusions. Adopted from Zinner et al. (2002).

The high transmission of the instrument also proved to be essential because of the low Mg content of the interesting analysis spots (Fig. 2). An initial $^{26}\text{Al}/^{27}\text{Al}$ ratio of $\sim 1.6 \times 10^{-7}$ is inferred for the time when the feldspar in Forest Vale formed. When this value is compared with the canonical value from CAI, an absolute age can be calculated. This age is in agreement with Pb-Pb ages of phosphates in the same meteorite. This suggests that ^{26}Al was indeed widely and uniformly distributed in the early solar system and can be used as a fine-scale chronometer.

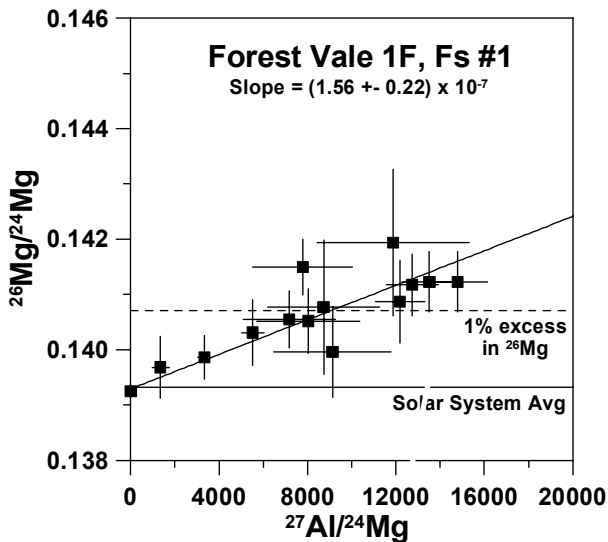


Fig. 2: Al-Mg systematics of Forest Vale plagioclase, according to Zinner et al. (2002). Errors are 1σ .

2.2. ^{53}Mn in Orgueil carbonates

Primitive meteorites, in particular carbonaceous chondrites of types CM and CI, show evidence for aqueous alteration. It is of great interest to ascertain when this aqueous activity occurred on the meteorite parent body. I-Xe analyses of halite (salt –one of the products of aqueous activity) in ordinary chondrites indicate that this formed very early in solar system

history (Whitby et al., 2000). But because of its rather long half-life the time resolution of the I-Xe chronometer (which is also plagued by other problems; cf. Ott, 2000) is limited. With very high Mn/Cr ratios in the carbonate products of aqueous alteration, ^{53}Mn - ^{53}Cr is a superior chronometer.

Preliminary (unpublished) data obtained with the Mainz NanoSIMS indicate the usefulness of the small beam diameter that allows to exclude Cr-rich inclusions and to analyze spots with $^{55}\text{Mn}/^{52}\text{Cr}$ ratios up to $\sim 50,000$. Compared to previous work (Endress et al., 1996; Hutchison et al., 1997) the Cr isotopic data are of higher precision. The inferred $^{53}\text{Mn}/^{55}\text{Mn}$ ratios of $\sim 3 \times 10^{-6}$ found for five carbonate grains from Orgueil are at the upper end of previously published values. The inferred absolute time of carbonate formation and, therefore, aqueous activity on the meteorite parent body is ~ 4563 Ma.

2.3. ^{60}Fe in the early solar system

Like ^{26}Al , ^{60}Fe is a potential heat source for melting asteroidal bodies in the early solar system. With its longer life time (~ 2 Ma) it is of special interest for the early development of Solar System bodies. The first demonstration of the existence in the early solar system of ^{60}Fe was obtained studying the HED meteorites by Shtukolyukov and Lugmair (1993). However, these meteorites are products of planetary differentiation and, therefore, are relatively young. The inferred $^{60}\text{Fe}/^{56}\text{Fe}$ ratio was $\sim 4 \times 10^{-9}$ at the time of their formation. Using the NanoSIMS, analyses of troilite (iron sulfide, which has suitably high Fe/Ni ratios) from one of the most primitive ordinary chondrites, Semarkona (Mostefaoui et al., 2003) has been performed. The preliminary inferred initial

$^{60}\text{Fe}/^{56}\text{Fe}$ ratio of $\sim 1 \times 10^{-6}$ is several times higher than the $1-2 \times 10^{-7}$ found by Tachibana and Huss (2003) in troilite from two other ordinary chondrites. At this abundance level ^{60}Fe may indeed have been an important heat source in the early solar system, its energy input exceeding that from ^{26}Al after $\sim 2-3$ Ma.

3. Pre-solar SiC studies

Among the pre-solar grains identified in meteorites SiC is the best-studied mineral type. Based on isotopic characteristics, SiC has been catalogued into different groups (Hoppe and Ott, 1997). Most abundant are the mainstream grains (>90%), which originate from AGB stars, and in which the heavy trace elements show the signature of the s-process. Another important subgroup is that of the X grains that probably derive from supernovae. Among other things, the X grains show strongly overabundant ^{28}Si , and many must have carried ^{44}Ti ($T_{1/2} = 60\text{a}$), which is revealed as an intense overabundance of its daughter, ^{44}Ca .

3.1. ^{44}Ti and ^{49}Ti in SiC X grains

Using the NanoSIMS, previous studies of ^{44}Ti in presolar SiC X grains have been expanded (Besmehn and Hoppe, 2003). The results largely agree with previous observations (Nittler et al., 1996; Hoppe et al., 2000; Besmehn 2001), however, analytical uncertainties are significantly reduced (Fig. 3).

The NanoSIMS also offers the possibility to study the distribution of excess ^{44}Ca (former ^{44}Ti) and its correlation with the element Ti. In one case at least, ^{44}Ti occurs localized and correlated with ^{48}Ti , suggestive of the occurrence

of TiC subgrains within SiC (lower row in Fig. 4).

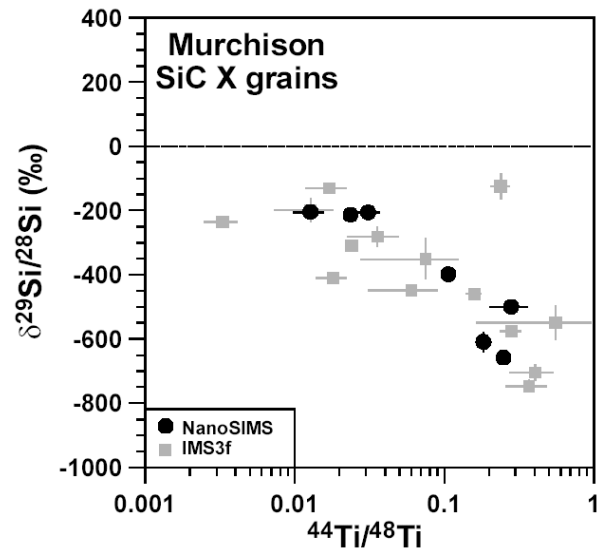


Fig.3. Correlation of inferred $^{44}\text{Ti}/^{48}\text{Ti}$ with Si isotopic composition in SiC X grains. The NanoSIMS data (black) confirm the trend seen in the data obtained with the Cameca IMS 3f (grey symbols), but have significantly higher precision. From: Besmehn and Hoppe (2003). Errors are 1σ .

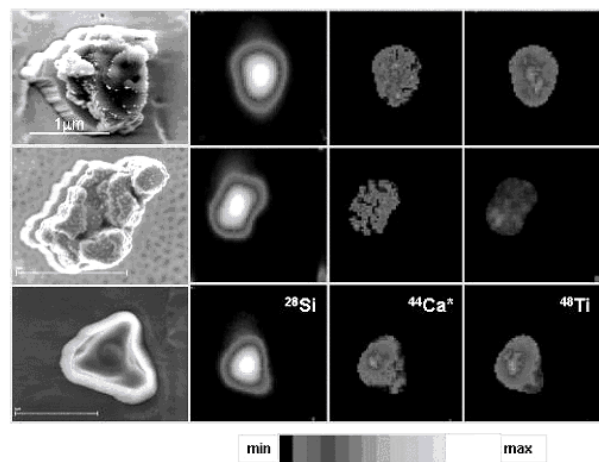


Fig. 4: Spatial distribution within SiC X grains of ^{28}Si , ^{44}Ca and ^{48}Ti (from: Besmehn and Hoppe, 2003). In contrast to the other two grains, the one at the bottom seems to contain a localized enrichment of ^{44}Ca that correlates with ^{48}Ti .

In yet another study of extinct radionuclides in presolar SiC X grains, evidence was found for the former presence of ^{49}V ($T_{1/2} = 331$ d), which puts constraints on the timescale of grain formation (Hoppe and Besmehn, 2002).

3.2. *s*-process Ba in SiC mainstream grains

A characteristic feature of mainstream SiC grains, which actually led to the identification and isolation of pre-solar SiC from meteorites, is the presence within them of heavy trace elements with a clear *s*-process signature. Thus, they are thought to be produced during the thermally pulsing stage of AGB stars (Hoppe and Ott, 1997). Since these trace elements typically occur on the level of ppm only, traditional isotope analyses have been performed on many SiC grains simultaneously (i.e. on “aggregates”), e.g. by noble gas mass spectrometry (e.g., Tang and Anders, 1988; Lewis et al., 1994), TIMS (e.g., Ott and Begemann, 1990; Prombo et al., 1993), and in one case SIMS (Zinner et al., 1991). Only recently has the development of the CHARISMA resonance ionization mass spectrometer (e.g., Nicolussi et al., 1997; Savina et al., 2003) made single grain analyses for such elements possible. Grain-to-grain variations are to be expected, because *s*-process elements will differ in their detailed isotopic composition depending on the star of origin and also on the exact stage of stellar evolution. The reason is that during the TP-AGB phase both the composition of the He-shell matter (where the *s*-process occurs) and the mixing ratio with (isotopically \sim normal) stellar envelope material will vary (e.g., Gallino et al., 1993; Savina et al., 2003).

In view of the enhanced sensitivity of the NanoSIMS compared to its predecessors, we are in the process of exploring its use for single

grain analyses of Ba (Marhas et al., 2003). Results as shown in Fig. 5 are quite comparable to those obtained by RIMS (Savina et al., 2003; see also Ott et al., 2003, this volume), indicating that for elements that are efficiently ionized and not seriously compromised by isobaric interferences, NanoSIMS is a simpler and more flexible alternative to RIMS (which is a one element at a time method).

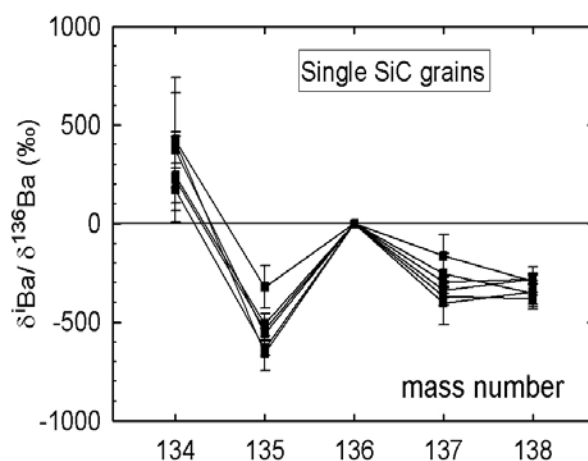


Fig. 5. Isotopic composition (relative to normal and ^{136}Ba) of Ba in individual presolar mainstream SiC grains. Data from Marhas et al. (2003).

4. Conclusions

The Cameca NanoSIMS 50 is a new generation ion microprobe that offers significantly improved capabilities in the study of pre-solar grains in meteorites and the decay products of extinct radioactivities in ancient solar system matter. Studies performed on solar system materials during the first two years of operation at the MPI for Chemistry, Mainz, include extinct ^{26}Al in ordinary chondrite feldspars, extinct ^{53}Mn in carbonates from the CI meteorite Orgueil, and extinct ^{60}Fe in

ordinary chondrite troilites. The NanoSIMS was also employed in the study of extinct ^{44}Ti and ^{49}V in pre-solar SiC grains from supernovae as well as s-process Ba in SiC mainstream grains from carbon stars. Some of these studies are still ongoing. Other projects in progress include the *in situ* search for presolar oxides and silicates in meteorite thin sections without the traditional chemical dissolution and isolation procedures (cf. Ott et al., 2003).

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