

A promising method to obtain more accurate Mg isotope compositional data on presolar silicate particles

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Due to their small grain size (200-300 nm) and chemical similarity to the host meteorite matrix, the isotope analysis of presolar silicate particles must be performed using in situ techniques, such as secondary ion mass spectrometry (SIMS). The achievable spatial resolution of analyses depends on the element of interest, and for Mg isotope measurements it is comparable to or exceeds the size of individual presolar silicate grains. This compromises isotope ratio measurements by dilution from the neighbouring matrix.

Here we present a method to prepare 200-300 nm presolar silicate grains of primitive meteorites for in situ isotope analysis with the NanoSIMS, a high spatial resolution secondary ion mass spectrometer, which minimises dilution effects imposed by the host meteorite matrix. This method follows the procedure developed by Nguyen et al. [A. N. Nguyen, S. Messenger, M. Ito, Z. Rahman, *Mg isotopic measurement of FIB-isolated presolar silicate grains*. 41st Lunar Planet Sci Conf, abstr. 2413] for dense grain separates.

Presolar silicate grains in a primitive carbonaceous chondrite (Acfer 094) were identified by their O isotope compositions, which can be measured at high spatial resolution (< 100 nm) with negligible dilution effect. After the grains had been identified in field-emission secondary electron microscope images, a focussed Ga ion beam was used to remove material around the grains in a 3 µm diameter circle to a depth of 1-1.5 µm, in order to minimise dilution effects. The major focus of our efforts has been the accurate analysis of Mg isotopes. Besides the potential of giving insight into nucleosynthetic processes affecting Mg isotope abundances, Mg isotope compositions of presolar silicate grains will also provide information on the Galactic chemical evolution of Mg.

*11th Symposium on Nuclei in the Cosmos - NIC XI
Heidelberg, Germany
July 19–23 2010*

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1. Introduction

Silicates are among the most abundant presolar particles found in primitive meteorites (e.g., [1]). Presolar silicate grains are rarely larger than 200-300 nm in the longest dimension and are either amorphous or crystalline (olivine, pyroxene). They are composed mostly of O, Si, Mg, Fe \pm Al \pm Ca [2; 3]. The isotope composition of presolar silicates can help to improve stellar nucleosynthesis models [4] and to better understand Galactic chemical evolution (GCE). Based on their oxygen isotope compositions most presolar silicate grains belong to Group 1 of the classification scheme of [5] (for a more concise overview on the classification of presolar oxide and silicate grains see the contribution by Peter Hoppe in this volume), suggesting that they formed in the stellar outflows of $M = 1.2-2.2 \times M_{\text{solar}}$ asymptotic giant branch stars with similar to or slightly higher than solar metallicity [6].

Due to their small grain size (200-300 nm) and chemical similarity to the host meteorite matrix, the isotope analysis of presolar silicates must be performed with the NanoSIMS, a mass spectrometer separating and detecting ions from a target material ejected due to irradiation by a primary ion beam on a spot as small as 50-400 nm. The achievable spatial resolution of NanoSIMS measurements depends on the element of interest: anions, such as O⁻, C⁻, N⁻ or Si⁻ can be analysed using a Cs⁺ primary ion source, which allows 50-150 nm spatial resolution, whereas measurements of most cations, such as Mg⁺ or Fe⁺, require an O⁻ primary ion beam which limits spatial resolution to about 200-400 nm, i.e. roughly the size of individual silicate stardust grains. Thus, Mg or Fe isotope measurements can be strongly affected by dilution by the isotope signal of neighbouring matrix material with solar system isotope composition, leading to inaccurate results.

In an effort to overcome this difficulty, Nguyen et al. [7] developed a grain preparation method for dense grain separates which allows more accurate isotope analysis of cations with the NanoSIMS by removing most of the material in the vicinity of grains with a focussed ion beam. We applied the same technique on a thick petrographic section of the ungrouped carbonaceous chondrite Acfer 094 [8]. Here we give a detailed description of the grain preparation method and report our first Mg isotope measurement results.

2. Preparation and isotope analysis of presolar silicate grains

2.1 Identification of presolar silicate grains

Presolar silicate grains were identified based on their combined O isotope and elemental composition with the NanoSIMS 50 at the Max Planck Institute for Chemistry. First, homogeneous fine-grained (average grain size < ~300 nm) portions of the meteorite matrix were selected for detailed isotope analyses. $10 \times 10 \mu\text{m}^2$ areas (54 in total) of the selected portions of the matrix were then scanned with a Cs⁺ primary ion beam (primary current: ~1 pA; beam diameter: ~100 nm). Secondary ions of ¹⁶O⁻, ¹⁷O⁻, ¹⁸O⁻, ²⁸Si⁺ and ²⁷Al¹⁶O⁻ were simultaneously detected, thereby allowing ion images to be generated (Fig. 1a). The acquired images were analysed: each grain that showed anomalous O isotope compositions with respect to the matrix (by more than 3 σ ; [9]) and had an O- and Si-rich but Al-poor composition qualified as presolar

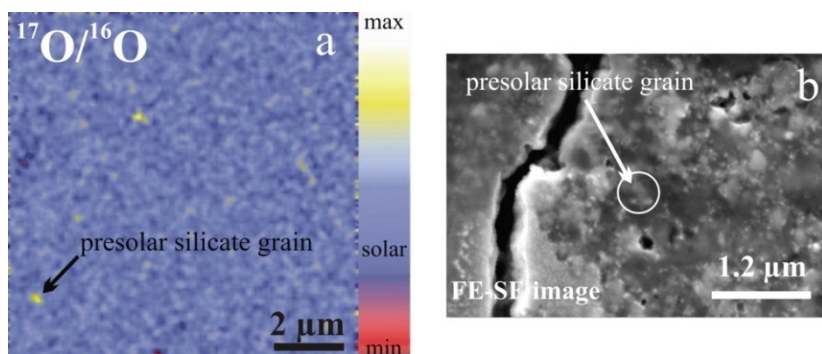


Figure 1: Identification of a presolar silicate grain based on its O isotope composition (a) followed by localisation of the grain in secondary electron images (b).

silicate. We identified 18 presolar silicate grains in the acquired 54 maps, from which 10 were selected for focussed ion beam (FIB) preparation and Mg isotope analysis. The selected grains belong to Group 1 based on their O isotope compositions [5].

Presolar silicate grains were subsequently localised on secondary electron (SE) images (Fig. 1b) recorded by a LEO 1530 field emission secondary electron microscope (FE-SEM). The selected grains are rounded or rectangular isometric to oval in the two dimensions of the thin section ranging in size from about $160 \times 160 \text{ nm}^2$ to $300 \times 390 \text{ nm}^2$.

2.2 Preparation with focussed ion beam

Focussed ion beam preparation was performed on the FEI Helios 600 instrument of the University of Saarland (Saarbrücken, Germany). First a 60-120 nm thick carbon cap was precipitated on the top of each selected presolar grain (Fig. 2a) against possible damage later by the FIB. Then ring-shaped areas around the grains were carved out stepwise (Fig. 2b) with a focussed Ga ion beam (acceleration voltage: 30 kV) such that the target presolar grain would be supported only by a 200-300 nm wide and 1-1.5 μm tall column of matrix by the end of the procedure (Fig. 2c). The inner diameter of the bombarded areas were decreased in each carving step, which required that the beam current also be reduced (from 0.28 nA to 1.5 pA) in order to achieve the required higher spatial resolution.

2.3 Mg isotope analyses

So far, Mg isotope analyses with the simultaneous measurements of Al and Si abundance were performed on two of the presolar silicate grains prepared with the FIB technique. $5 \times 5 \mu\text{m}^2$ areas which included the prepared grains (Fig. 3a) and their vicinity were scanned with an O^- primary beam (primary current: 1-2 pA; beam diameter: $\sim 200 \text{ nm}$, 68% of beam intensity) and signals of secondary $^{24}\text{Mg}^+$, $^{25}\text{Mg}^+$, $^{26}\text{Mg}^+$, $^{27}\text{Al}^+$ and $^{28}\text{Si}^+$ were collected simultaneously to generate 256×256 pixel isotope images (Figs. 3b and c). We considered the protective carbon cap to be destroyed as soon as the ^{28}Si signal from the grain was comparable to that of matrix silicates (which had no protective carbon layer). The Mg isotope ratios of each presolar silicate grain were then normalised to the Mg isotope ratios of the neighbouring matrix, which is likely to have an Mg isotope composition similar to solar. Thus, deviations in the abundances of Mg

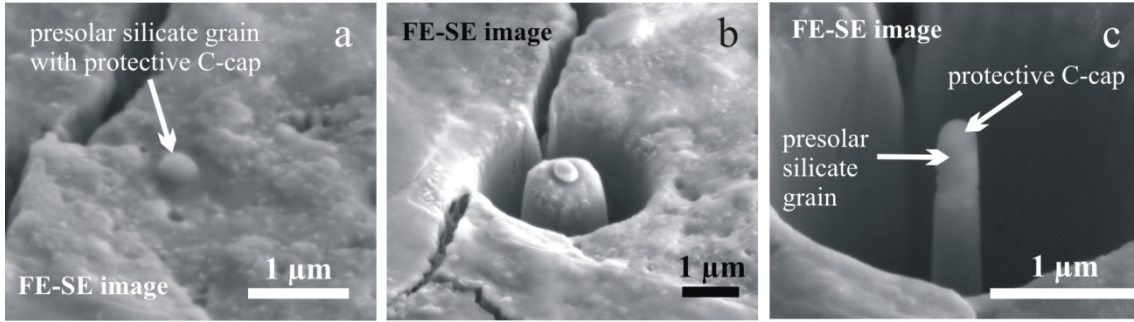


Figure 2: Stepwise preparation of a presolar silicate grain with the FIB (see text for details).

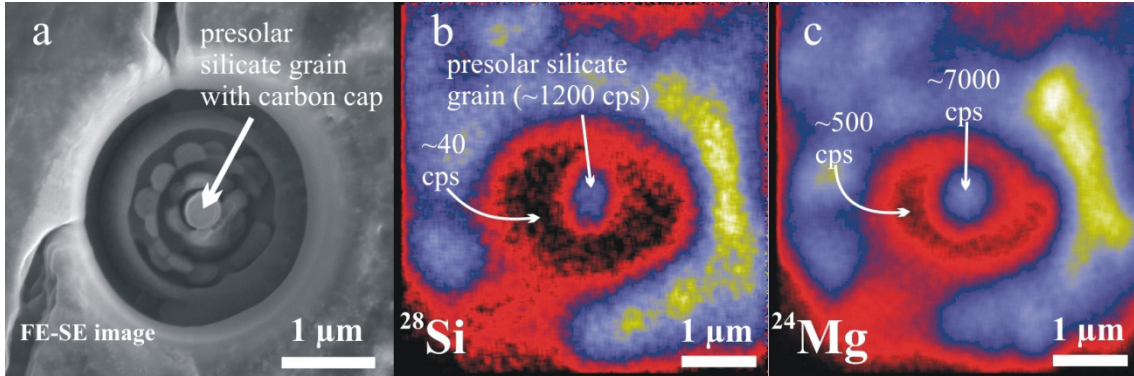


Figure 3: Secondary electron (a) and isotope images (b and c; “cps” = counts per second) of a presolar silicate grain prepared by the FIB technique. Secondary ion emission and transmission is well known to be affected by sample topography. Isotope signals are significantly weaker in the area carved out around the grain, which is essential for the application of our method.

isotopes in the presolar grains relative to solar isotope abundances can be quantified and expressed as $\delta^x\text{Mg}$ ($\delta^x\text{Mg} = 1000 \times [((^x\text{Mg}/^{24}\text{Mg})_{\text{grain}}/(^x\text{Mg}/^{24}\text{Mg})_{\text{matrix}}) - 1]$; where $x = 25$ or 26 ; Table 1).

The two silicate grains we have analyzed so far for Mg isotopes (Table 1) have solar $^{25}\text{Mg}/^{24}\text{Mg}$ ($\delta^{25}\text{Mg} = -9 \pm 17 \text{‰}$ and $11 \pm 17 \text{‰}$). The $^{26}\text{Mg}/^{24}\text{Mg}$ of one grain was solar as well ($\delta^{26}\text{Mg} = -13 \pm 16 \text{‰}$), whereas the other grain's $^{26}\text{Mg}/^{24}\text{Mg}$ is $>2\sigma$ higher than solar with $\delta^{26}\text{Mg} = 35 \pm 16 \text{‰}$. This could be due to, e.g., GCE or due to in situ decay of ^{26}Al . If increased $^{26}\text{Mg}/^{24}\text{Mg}$ were solely related to in situ ^{26}Al -decay, then an initial $^{26}\text{Al}/^{27}\text{Al}$ ratio of 0.016 ± 0.006 could be calculated for the ^{26}Mg -enriched grain. The calculated initial $^{26}\text{Al}/^{27}\text{Al}$ ratio is at the upper end of compositions found in group 1 oxide grains [10], but lower than the value of 0.12 inferred for a group 2 silicate grain [11] and in many group 2 oxide grains [10].

Table 1 Oxygen and Mg isotope compositions of presolar silicate grains of Acfer 094

Grain code	$^{17}\text{O}/^{16}\text{O}$ (10^{-4})	$^{18}\text{O}/^{16}\text{O}$ (10^{-4})	$\delta^{25}\text{Mg}$ (‰)	$\delta^{26}\text{Mg}$ (‰)
acfer094_03a_04_01	7.32 ± 0.49	19.24 ± 0.79	11 ± 17	35 ± 16
acfer094_03a_addim02_02	10.19 ± 0.63	19.51 ± 0.87	-9 ± 17	13 ± 16

3. Implications and outlook

The ^{26}Mg -enriched presolar silicate grain would have been considered to have a solar $^{26}\text{Mg}/^{24}\text{Mg}$ if it had not been prepared with the FIB, as described here. Assuming that (1) this grain had a spherical shape which was exposed at its equator prior to Mg isotope analysis, that (2) there was only negligible difference between the chemical composition and density of this grain and the surrounding matrix and (3) that the spatial resolution of Mg isotope measurements is 300 nm (95 % of beam intensity), the ^{26}Mg -enriched grain would have shown a $\delta^{26}\text{Mg}$ of about 16 ‰, i.e. indistinguishable from the matrix within measurement uncertainties.

The preparation method described here is thus very promising for future NanoSIMS isotope analyses of presolar silicates. The analysis of cations, which requires an O^- primary beam providing poorer spatial resolution, can be measured more accurately after preparation with the FIB. One of the potential elements whose isotope analysis can certainly benefit from the new preparation method is Fe, present in several weight % in presolar silicate grains [2].

Acknowledgements - We thank Fabio Soldera and Christoph Pauly (University of Saarland) for their help with the FIB. We are also grateful to Joachim Huth and Elmar Gröner (Max Planck Institute for Chemistry, Mainz) for their assistance with the SEM and the NanoSIMS, respectively. The review comments of Ernst Zinner have greatly improved the manuscript.

References

- [1] P. Hoppe (2008), *Reservoir for Comet Material: Circumstellar Grains*, Space Sci Rev **138**, 43-57
- [2] C. Floss, Stadermann F (2009), *Auger Nanoprobe analysis of presolar ferromagnesian silicate grains from primitive CR chondrites QUE 99177 and MET00426*. GCA **73**, 2415-2440
- [3] C. Vollmer, P. Hoppe, F. J. Stadermann, C. Floss, F. E. Brenker (2009), *NanoSIMS analysis and Auger electron spectroscopy of silicate and oxide stardust from the carbonaceous chondrite Acfer 094*. GCA **73**, 7127-7149
- [4] C. Vollmer, P. Hoppe, F. E. Brenker (2008), *Si isotopic compositions of presolar silicate grains from red giant stars and supernovae*. Astrophys J **684**, 611-617
- [5] L. R. Nittler, C. M. O'D. Alexander, X. Gao, R. M. Walker, E. K. Zinner (1994), *Interstellar oxide grains from the Tieschitz ordinary chondrite*. Nature **370**, 443-446
- [6] A. I. Boothroyd, I.-J. Sackmann (1999), *The CNO isotopes: Deep circulation in red giants and first and second dredge-up*. Astrophys J **510**, 232-250
- [7] A. N. Nguyen, S. Messenger, M. Ito, Z. Rahman (2010), *Mg isotopic measurement of FIB-isolated presolar silicate grains*. 41st Lunar Planet Sci Conf, abstr. 2413
- [8] J. Newton, A. Bischoff, J. W. Arden, I. A. Franchi, T. Geiger, A. Greshake, C. T. Pillinger (1995), *Acfer 094, a uniquely primitive carbonaceous chondrite from the Sahara*. Meteoritics **30**, 47-56
- [9] S. Mostefaoui, P. Hoppe (2004), *Discovery of abundant in situ silicate and spinel grains from red giant stars in a primitive meteorite*. Astrophys J **613**, L149-L152
- [10] L. R. Nittler, C. M. O'D. Alexander, R. Gallino, P. Hoppe, A. N. Nguyen, F. J. Stadermann, E. K. Zinner (2008), *Aluminium-, calcium- and titanium-rich oxide stardust in ordinary chondrite meteorites*. Astrophys J **682**,:1450-1478
- [11] A. N. Nguyen, E. K. Zinner (2004), *Discovery of Ancient Silicate Stardust in a Meteorite*. Sci **303**, 1496-1499