

SULFUR IN PRESOLAR SILICON CARBIDE GRAINS FROM ASYMPTOTIC GIANT BRANCH STARS.

P. Hoppe¹, K. Lodders², W. Fujiya¹, and E. Gröner¹, ¹Max Planck Institute for Chemistry, P.O. Box 3060, 55020 Mainz, Germany (peter.hoppe@mpic.de), ²Dept. of Earth & Planetary Sciences, Campus Box 1169, Washington University, St. Louis, MO 63130, USA.

Introduction: Primitive solar system materials contain small quantities of presolar grains that formed in the winds of evolved stars or in the ejecta of stellar explosions [1]. The SiC grains are the best characterized presolar mineral. Most of these grains belong to the mainstream (MS) population which formed in the winds of 1-3 M_{\odot} asymptotic giant branch (AGB) stars of about solar metallicity. The type AB SiC grains have $^{12}\text{C}/^{13}\text{C}$ ratios <10 and constitute a few % of all SiC grains. Their origins is still a matter of debate. Among the proposed stellar sources are J-type carbon stars and born-again AGB stars, such as Sakurai's object [2]. Recent S isotope measurements of AB grains revealed significant ^{32}S enrichments (~ 250 ‰) in 3 grains. Born-again AGB stars are predicted to produce significant amounts of radioactive ^{32}Si (half life: 153 yr) and the ^{32}S excesses may be the result of ^{32}Si decay [3], which was proposed for the SiC type C grains of supernova origin [4]. To substantiate this possibility further, it is necessary to identify more AB grains for further S isotope measurements, to evaluate the effects of Galactic chemical evolution (GCE) on S-isotopic compositions that may be recorded in MS grains, and to investigate the condensation behavior of S into SiC.

We present results from (i) a search for a large number of AB grains by automated C and Si ion imaging which will be studied for S-isotopic compositions later, (ii) measurements of S-isotopic compositions and abundances of SiC MS grains, and (iii) condensation calculations for S into SiC.

Experimental: The SiC grains were separated from a 48 g sample of the Murchison CM2 meteorite using a procedure similar to that of [5]. Thousands of grains were deposited from liquid suspension onto two clean Au foils (samples "Mur2012B-3/4"). By ion imaging with the MPI NanoSIMS (Cs^+ primary ions, ~ 100 nm beam size, ~ 1 pA) [6] we measured the C- and Si-isotopic compositions of ~ 1100 SiC grains found in 347 $30 \times 30 \mu\text{m}^2$ -sized areas. Additional areas not screened by ion imaging were inspected in the SEM. This led to the identification of 59 large ($>1 \mu\text{m}$) grains of which 23 were measured for C- and Si-isotopic compositions by recording high-resolution images of ^{12}C , ^{13}C , ^{28}Si , ^{29}Si , and ^{30}Si ($2.9 \times 2.9 \mu\text{m}^2$, Cs^+ primary ions, ~ 1 pA). After intense pre-sputtering for cleaning, the S-isotopic compositions were measured for 9 of these grains (all of MS type) by acquiring

high-resolution images of $^{28}\text{Si}^-$, $^{32}\text{S}^-$, $^{33}\text{S}^-$, and $^{34}\text{S}^-$ with long integration times (~ 160 min/grain, divided into 30 image planes). Sulfur isotope data were normalized to those of S impurities in a synthetic SiC standard.

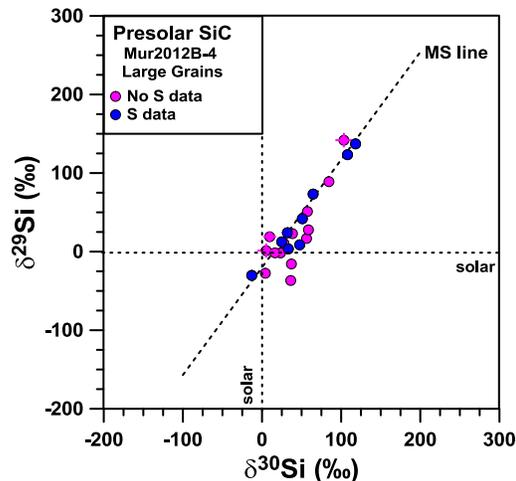


Figure 1. Si-isotopic compositions of large (1-6 μm) presolar SiC grains from Murchison sample Mur2012B-4. Errors are 1σ . MS line: $\delta^{29}\text{Si} = -20 + 1.37 \times \delta^{30}\text{Si}$ [7].

Results and Discussion: Forty-two AB grains were found by ion imaging, representing 3.8% of all measured SiC grains. Ion imaging revealed one interesting C grain (~ 250 nm) with $^{12}\text{C}/^{13}\text{C} = 68 \pm 1$, $\delta^{29}\text{Si} = 490 \pm 14$ ‰, and $\delta^{30}\text{Si} = 2135 \pm 26$ ‰. All of the large grains have Si-isotopic compositions along the characteristic MS line (Fig. 1), and $^{12}\text{C}/^{13}\text{C}$ ratios between 3 and 134.

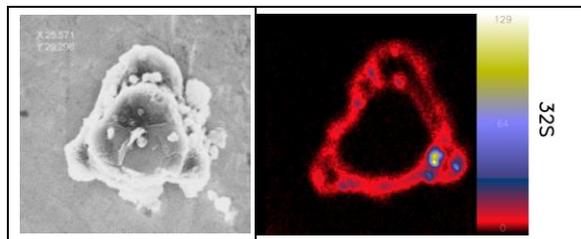


Figure 2. SEM image and corresponding $^{32}\text{S}^-$ NanoSIMS ion image of grain Mur2012B-4-26. FoV: $4 \times 4 \mu\text{m}^2$.

Contamination by S on or in very close proximity of individual SiC grains complicated S isotope measurements. To minimize the S contamination problem we considered only those areas in the ion images for

the data reduction that apparently have no or only small contributions from S contamination (Fig. 2). One grain with a very rough surface texture still shows a very high S concentration and will not be considered in the following discussion. The S isotope and abundance data of 8 grains (for one grain only $^{34}\text{S}/^{32}\text{S}$ data are available) are shown in Figs. 3 and 4. Visual inspection of Fig. 3 suggests a positive correlation between $\delta^{33}\text{S}$ and $\delta^{34}\text{S}$. However, a statistical treatment of the data shows only moderate statistical significance, with a confidence level of 75% for a slope >1 . Mass-weighted averages are $\delta^{33}\text{S} = -9 \pm 56 \text{ ‰}$ and $\delta^{34}\text{S} = 11 \pm 23 \text{ ‰}$. Close-to-solar S isotope compositions are in general agreement with S isotope data for 9 very large SiC grains from the Murchison LS + LU series [8], and with predictions for the 3rd dredge-up in 1.5-3 M_{\odot} AGB stars of solar metallicity ($\delta^{33}\text{S} = 10\text{-}51 \text{ ‰}$, $\delta^{34}\text{S} = 6\text{-}17 \text{ ‰}$ for the final pulse [9]).

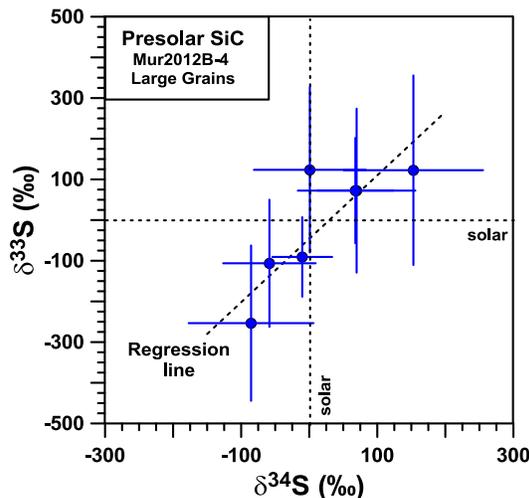


Figure 3. S-isotopic compositions of 8 MS grains from this study. Errors are 1σ . The regression line has a slope of ~ 1.5 .

The S isotope data in the single grains have larger errors so they are not very diagnostic for the range of S-isotopic ratios in their parent stars and for GCE modeling. We now discuss the elemental S abundances. Using equilibrium condensation calculations [10] the observed S abundances of MS grains can be reproduced, e.g., at $C/O = 1.05$, $p = 10^{-5}$ bar, and $T \sim 1400$ K (Fig. 4). This assumes ideal solid solution of CaS (major) and MgS (minor) in SiC; and that sulfides do not form as pure phases. If the solution is not ideal, the calculated amounts of CaS are too high and predicted S/Si ratios represent upper limits; the same results if CaS (& MgS) condense separately from SiC. The inferred temperature is ~ 100 K higher than what was inferred for other trace elements in SiC [10], indicating that ideal solution does not apply, that separate for-

mation of CaS and MgS occurred, or both. The predicted S/Si ratios strongly depend on T and a decrease by 100 K even matches the 100x higher S abundances of AB grains with the ^{32}S excesses [3]. If conditions for condensation in born-again AGB stars are comparable to that in normal AGB stars then a 100x higher S abundance in AB grains is hard to understand. Unlike born-again AGB stars, the AGB parent stars of MS grains can only produce tiny levels of ^{32}Si [9] and direct condensation of S into SiC is the most plausible origin of S in the grains. The low levels of S in MS grains provide further evidence that ^{32}S excesses in AB grains are not the S-isotopic signature of their parent stars but are best explained by a mixture of radiogenic ^{32}S (from in situ ^{32}Si decay after formation of SiC with $^{32}\text{Si}/^{28}\text{Si} \sim 10^{-3}$) and isotopically normal S, mostly contamination. The high level of S contamination in AB grains is consistent with their smaller size, which did not allow for an extensive cleaning before analysis.

Acknowledgements: We thank Antje Sorowka and Joachim Huth for SEM analyses, and the Field Museum Chicago for providing the Murchison sample. Work by KL supported by NSF AST 0807356.

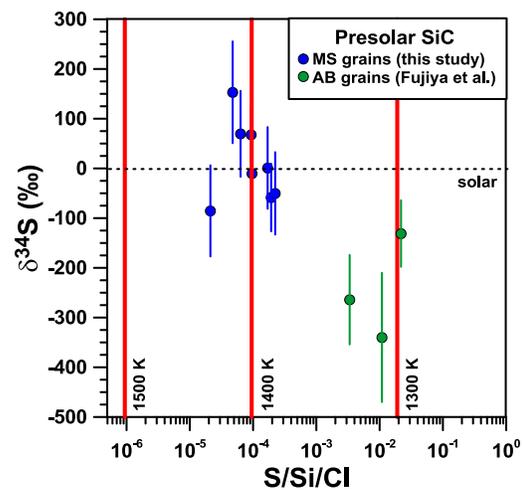


Figure 4. $\delta^{34}\text{S}$ as function of CI-normalized S/Si ratios of 8 MS grains (this study) and of 3 AB grains [3]. Errors are 1σ . Red lines: S/Si/CI ratios from equilibrium condensation calculations for different T at $p = 10^{-5}$ bar and $C/O = 1.05$.

References: [1] Zinner E. (2014) In *Meteorites and Cosmochemical Processes*, Chapter 1.4 (ed. A. M. Davis), pp. 181. [2] Asplund M. et al. (1999) *A&A*, 343, 507. [3] Fujiya W. et al. (2013) *ApJ*, 776, L29. [4] Pignatari M. et al. (2013) *ApJ*, 771, L7. [5] Amari S. et al. (1994) *GCA*, 58, 459. [6] Gröner E. & Hoppe P. (2006) *Appl. Surf. Sci.*, 252, 7148. [7] Zinner E. et al. (2007) *GCA*, 71, 4786. [8] Gyngard F. et al. (2007) *LPSC*, 38, #1963. [9] Cristallo S. et al. (2009) *ApJ*, 696, 797. [10] Lodders K. & Fegley B. (1995) *Meteoritics*, 30, 661.