

SULFUR-ISOTOPIC SIGNATURE OF PRESOLAR SiC GRAINS OF TYPE X. P. Hoppe¹ and E. Zinner²,
¹Max Planck Institute for Chemistry, P.O. Box 3060, 55020 Mainz, Germany (peter.hoppe@mpic.de), ²Laboratory for Space Sciences and Physics Dept., Campus Box 1105, 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]. SiC is the best characterized presolar mineral. Most of these grains formed in the winds of 1-3 M_{\odot} AGB stars. SiC X and U/C grains, which constitute about 1-2% of presolar SiC grains, are from Type II supernovae (SNeII). This is evidenced by specific isotopic fingerprints, e.g., isotopically light (X grains) or heavy (U/C grains) Si and the initial presence of now extinct ^{44}Ti (half life 60 y) [2, 3]. An important signature of U/C grains are large enrichments in ^{32}S [3-5]. Simple ad hoc SNII mixing models cannot account for heavy Si together with light S, as observed in U/C grains. The isotope data suggest preferential trapping of S from the inner Si/S zone over S from other zones [3]. A way to achieve this is by molecule chemistry in SNII ejecta. SiS is predicted to form efficiently in the still unmixed ejecta from the Ni/Si/S zone [6] and it was argued that the S isotope signatures of U/C grains can be explained if SiS is much more efficiently captured by the growing SiC grains than atomic S or other S-bearing molecules from other zones [3].

Here, we report results of S isotope measurements on X grains made in order to gain further insights into the S-isotopic signature of SN dust and the chemical and physical processes taking place in SNII ejecta.

Experimental: The SiC grains of this study were separated from the Murchison CM2 meteorite [7] and deposited from liquid suspension onto a clean Au foil (sample "M7"). Areas suitable for NanoSIMS ion imaging were selected in the Leo 1530 FE-SEM at the MPI for Chemistry. In the WU NanoSIMS ion probe we measured the C- and Si-isotopic compositions (Cs^+ primary ions, ~ 100 nm beam size, ~ 1 pA) of ~ 2300 SiC grains found in 464 $20 \times 20 \mu\text{m}^2$ -sized areas with an automatic grain mode program [8]. Sulfur-isotopic compositions were measured on 22 X grains by recording high-resolution images of $^{28}\text{Si}^-$, $^{32}\text{Si}^-$, $^{33}\text{Si}^-$, and $^{34}\text{Si}^-$ ($1.5\text{-}3 \times 1.5\text{-}3 \mu\text{m}^2$, Cs^+ primary ions, ~ 1 pA) with the WU and MPI NanoSIMS ion probes.

Results and Discussion: Twenty-five X grains were found during the automatic search, having $\delta^{29}\text{Si}$ values between -90 and -570 ‰, $\delta^{30}\text{Si}$ values between -200 and -700 ‰ (Fig. 1), and $^{12}\text{C}/^{13}\text{C}$ ratios from 25 to 1080. These ranges as well as the X grain abun-

dance of $\sim 1\%$ agree with the results of previous studies [4, 9, 10].

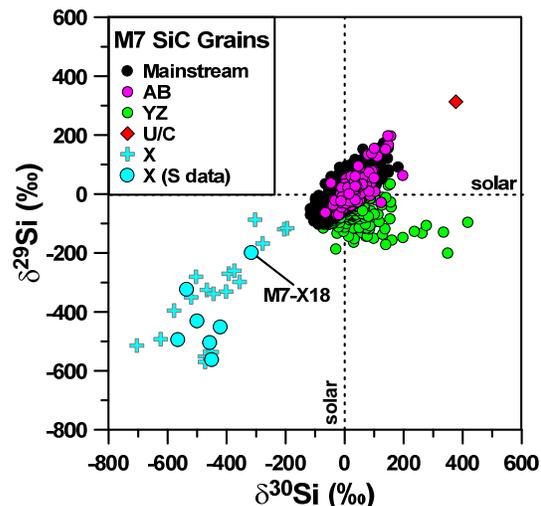


Figure 1. Si-isotopic compositions of different populations of presolar SiC grains from Murchison sample M7. Light-blue circles represent data for the X grains shown in Fig. 3.

Contamination by S on or very close to individual X grains complicated S isotope measurements and the data are likely to be affected by varying contributions of terrestrial S. For six X grains the S signal was clearly dominated by contamination, as evidenced from the spatial distribution of S and Si in the ion images. For the remaining 16 X grains the problem was less severe, though still present (Fig. 2). Although S hotspots were excluded before calculating S-isotopic ratios, intrinsic S-isotopic signatures are likely significantly more extreme than measured. Despite these problems, in one case (M7-X18) a clear excess in ^{32}S was seen and also most of the remaining grains tend to have isotopically light S (Fig. 3). Even if grain M7-X18 ($\delta^{33}\text{S} = -356 \pm 114$ ‰, $\delta^{34}\text{S} = -209 \pm 53$ ‰, ~ 1 wt% S) is excluded, mass-weighted averages of $\delta^{33}\text{S}$ (-70 ± 33 ‰) and $\delta^{34}\text{S}$ (-32 ± 14 ‰) in the remaining 15 grains are anomalous $>2\sigma$.

With SNII ad hoc mixing, using the $15 M_{\odot}$ model of [11], it is possible to reproduce the Si- and C-isotopic compositions of grain M7-X18 ($\delta^{29}\text{Si} = -199 \pm 5$ ‰, $\delta^{30}\text{Si} = -317 \pm 6$ ‰, and $^{12}\text{C}/^{13}\text{C} = 131 \pm 2$). Mixing matter from the Si/S : O/Si : O/Ne : O/C : He/C : He/N : H zones in the proportions 0.0047 : 0.0026 : 0.0125 : 0 : 0.228 : 0.134 : 0.618 results in

$\delta^{29}\text{Si} = -198 \text{ ‰}$, $\delta^{30}\text{Si} = -313 \text{ ‰}$, and $^{12}\text{C}/^{13}\text{C} = 131$. For S it results in $\delta^{33}\text{S} = -459 \text{ ‰}$ and $\delta^{34}\text{S} = -413 \text{ ‰}$, the fingerprint of the Si/S zone (Fig. 4). There is clear indication for S contamination around M7-X18 (Fig. 2) and some of the S in the grain might be contamination as well. If assuming about 40% contaminating S it is possible to reproduce the S-isotopic composition of X18.

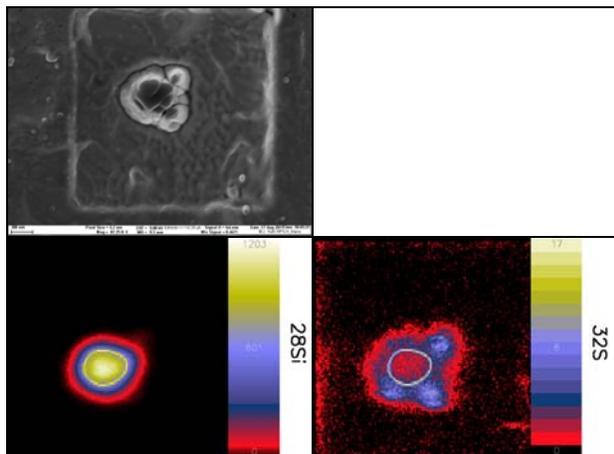


Figure 2. SEM picture, and $^{28}\text{Si}^-$ and $^{32}\text{Si}^-$ ion images ($2 \times 2 \mu\text{m}^2$) of X grain M7-X18.

It has been argued that S from the Si/S zone must be more efficiently trapped than S from other zones to account for the Si and S isotope data of U/C grains [3]. If we consider a fractionation factor of 50 between S from the Si/S zone and S from the other zones we obtain $\delta^{33}\text{S} = -792 \text{ ‰}$ and $\delta^{34}\text{S} = -865 \text{ ‰}$ in the mixture considered above. In this scenario, about 70% of contaminating S would be required to account for the observed S-isotopic composition of M7-X18.

Higher relative contributions from the Si/S zone imply larger ^{32}S enrichments in X than in U/C grains, which has not been seen. However, as we have pointed out, S contamination is a serious and unavoidable problem that might have lowered intrinsic S isotope anomalies to varying degrees. It is possible that in X grains the invoked S fractionation for U/C grains is smaller and intrinsic S concentrations lower. Anyhow, the finding of ^{32}S enrichments in X grains confirms SN model predictions of light S in the Si/S zone. This lends support to the conclusion that U/C grains have preserved a record of S molecule chemistry in their parent SNII ejecta [3].

Acknowledgements: We thank J. Huth for SEM analyses, E. Gröner and T. Smolar for technical support on the NanoSIMS, F. Gyngard for the automatic grain mode program, and Y. Xu for her help during ion imaging. PH thanks R. Cowdik for his hospitality at the McDonnell Center for the Space Sciences and EZ acknowledges support from NASA's cosmochemistry program.

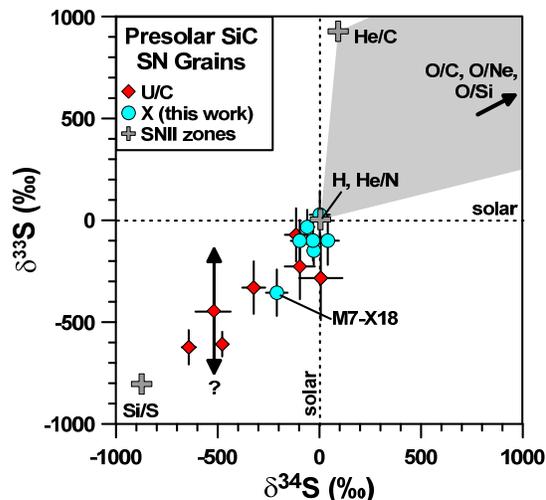


Figure 3. S-isotopic compositions of SiC SN grains and of the different zones in a $15 M_{\odot}$ SNII [11]. X grain data are only shown if the error in $\delta^{33}\text{S}$ is less than 150 ‰ .

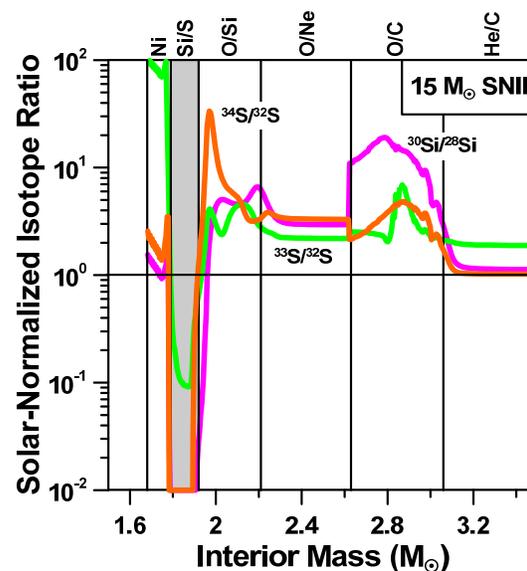


Figure 4. Model predictions of solar-normalized $^{30}\text{Si}/^{28}\text{Si}$, $^{33}\text{S}/^{32}\text{S}$, and $^{34}\text{S}/^{32}\text{S}$ ratios in a $15 M_{\odot}$ SNII [11].

References: [1] Zinner E. (2007) in *Treatise on Geochemistry, Vol. 1* (eds. A. Davis et al.), 1. [2] Nittler L. R. et al. (1996) *ApJ*, 462, L31. [3] Hoppe P. et al. (2012) *ApJL*, in press. [4] Hoppe P. et al. (2010) *ApJ*, 719, 1370. [5] Gyngard F. et al. (2010) *MNRAS*, 405, A72. [6] Cherchneff I. & Dwek E. (2009) *ApJ*, 703, 642. [7] Besmehn A. & Hoppe P. (2003) *GCA*, 67, 4693. [8] Gyngard F. et al. (2010) *ApJ*, 717, 107. [9] Nittler L. R. & Alexander C. M. O'D. (2010) *GCA*, 67, 4961. [10] Zinner E. et al. (2007) *GCA*, 71, 4786. [11] Rauscher T. et al. (2002) *ApJ*, 576, 323.