

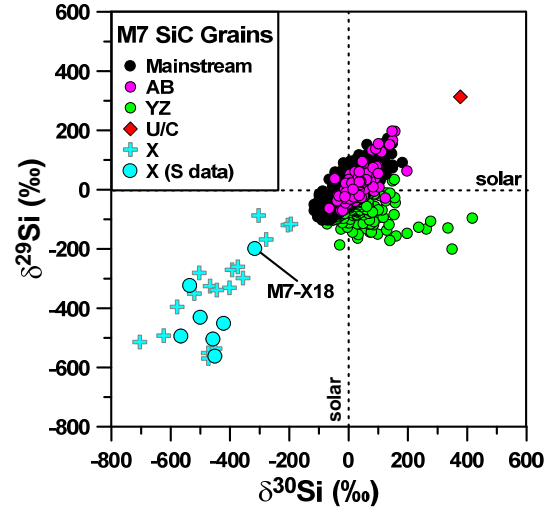
**Introduction:** Primitive solar system materials contain small quantities of presolar grains that formed in the winds of evolved stars or in the ejecta of stellar explosions [1]. SiC is the best characterized presolar mineral. Most of these grains formed in the winds of 1-3  $M_{\odot}$  AGB stars. 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  $^{44}\text{Ti}$  (half life 60 y) [2, 3]. An important signature of U/C grains are large enrichments in  $^{32}\text{S}$  [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 ( $\text{Cs}^+$  primary ions,  $\sim 100$  nm beam size,  $\sim 1$  pA) of  $\sim 2300$  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  $^{34}\text{Si}^-$  ( $1.5\text{-}3 \times 1.5\text{-}3 \mu\text{m}^2$ ,  $\text{Cs}^+$  primary ions,  $\sim 1$  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].

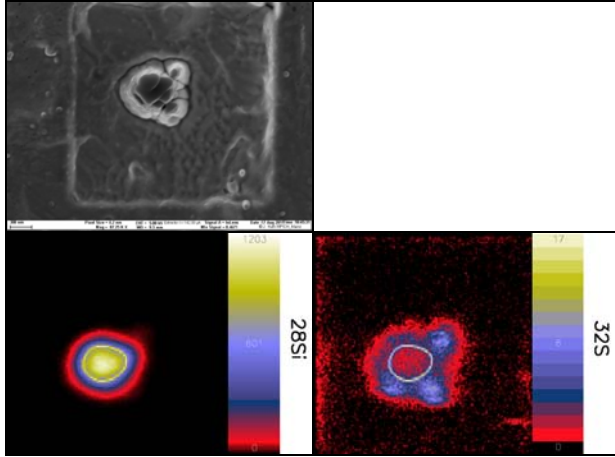


**Figure 1.** Si-isotopic compositions of different populations of presolar SiC grains from Murchison sample M7. Light-blue circles represent data for the X grains shown in Fig. 3.

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  $^{32}\text{S}$  was seen and also most of the remaining grains tend to have isotopically light S (Fig. 3). Even if grain M7-X18 ( $\delta^{33}\text{S} = -356 \pm 114$  ‰,  $\delta^{34}\text{S} = -209 \pm 53$  ‰,  $\sim 1$  wt% S) is excluded, mass-weighted averages of  $\delta^{33}\text{S}$  ( $-70 \pm 33$  ‰) and  $\delta^{34}\text{S}$  ( $-32 \pm 14$  ‰) 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.

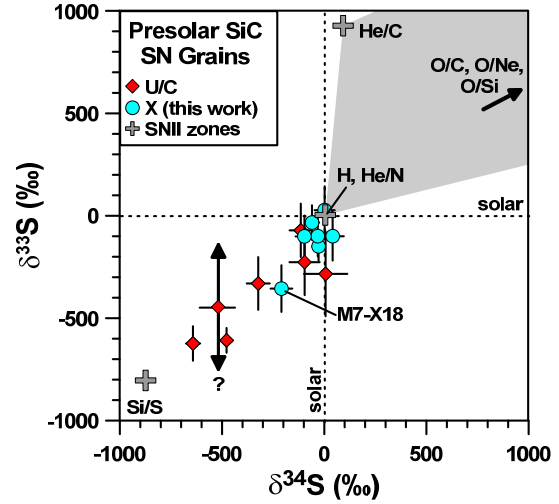


**Figure 2.** SEM picture, and  $^{28}\text{Si}^+$  and  $^{32}\text{Si}^+$  ion images ( $2 \times 2 \mu\text{m}^2$ ) of X grain M7-X18.

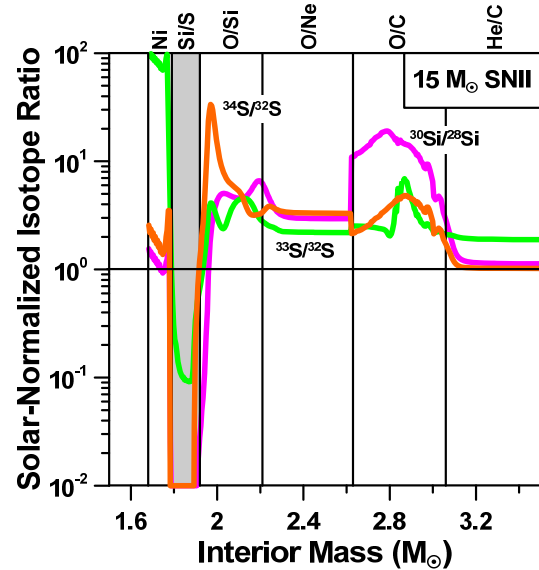
It has been argued that S from the Si/S zone must be more efficiently trapped than S from other zones to account for the Si and S isotope data of U/C grains [3]. If we consider a fractionation factor of 50 between S from the Si/S zone and S from the other zones we obtain  $\delta^{33}\text{S} = -792 \text{ ‰}$  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  $^{32}\text{S}$  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  $^{32}\text{S}$  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].

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**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  $150 \text{ ‰}$ .



**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) *MAPS*, 45, 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.