TITANIUM-44 AND LIGHT SULFUR IN PRESOLAR SILICON CARBIDE GRAINS WITH HEAVY SILICON: PROOF OF A SUPERNOVA ORIGIN.

P. Hoppe[1] and W. Fujiya[2], [1]Max Planck Institute for Chemistry, P.O. Box 3060, 55020 Mainz, Germany (peter.hoppe@mpic.de), [2]Dep. of Earth and Planetary Science, University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-0033, Japan.

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 grains, which constitute about 1% of the SiC grains, are from Type II supernovae (SNeII). This is evidenced from specific isotopic fingerprints, e.g., isotopically light Si and presence of now extinct ^{44}Ti (half life 60 y). Other SiC grains with likely SNII origin are grains with isotopically heavy Si (δ^{29}Si > 250 ‰) [2-6]. These rare grains have been named "unusual" [5] or "Type C" [6] and are found predominantly among the smallest grains. Two of these grains were shown to carry large S isotope anomalies, namely, enrichments in ^{32}S [5,6]. Simple ad-hoc SNII mixing models can not account for heavy Si together with light S, pointing to deficiencies in our current understanding of SN mixing and chemistry [5].

Here, we report on a search for further SiC grains with heavy Si. In addition to Si, we also measured C, S, Mg-Al, and Ca-Ti isotopic compositions in order to get new insights into the stellar sources of these grains. This search was conducted together with a search for X grains which were studied for Li and B isotopes [7].

Experimental: By NanoSIMS ion imaging (Cs$^+$ primary ions, ~100 nm beam size, ~1 pA) [8] we measured the C- and Si-isotopic compositions of ~1100 SiC grains separated from the Murchison meteorite at MPI for Chemistry [9]. Four grains with heavy Si, with sizes between 250 nm and 1 µm, were subsequently imaged (3 x 3 µm^2, Cs$^+$ primary ions) for ^{33}S/^{32}S and ^{34}S/^{32}S ratios. The two largest grains were measured in addition for Mg-Al isotopic compositions and for ^{40}Ca, ^{42}Ca, ^{44}Ca, and ^{48}Ti using O$^-$ primary ions (~400 nm beam size, 1-5 pA, 3-7 x 3-7 µm^2-sized images). The sensitivity factors used to infer ^{26}Al/^{27}Al were taken from [5] (ε(Al$^+$)/(ε(Mg$^+$) = 1.56) and for ^{44}Ti/^{48}Ti from [9] (ε(Ti$^+$)/(ε(Ca$^+$) = 0.51).

Results and Discussion: In Table 1 we list the isotope ratios of the four SiC grains with heavy Si of this study. Their Si- and S-isotopic compositions are displayed in Figs. 1-3 together with those of previously found grains [2-6]. The new grains exhibit enrichments in ^{29}Si and ^{30}Si of about a factor of 2. Grains C and D show large S isotope anomalies with enrichments in ^{32}S of more than a factor of 2; their Mg is essentially monoisotopic ^{26}Mg from which ^{26}Al/^{27}Al ratios of 0.015 and 0.12 are inferred. Grains C and D have normal ^{42}Ca/^{40}Ca but large excesses in ^{44}Ca, indicative of the decay of radioactive ^{44}Ti. Inferred ^{44}Ti/^{48}Ti ratios are 0.013 ± 0.002 and 0.077 ± 0.002.

Table 1. SiC grains with heavy Si from this study.

Grain	^{12}C/^{13}C	δ^{29}Si (‰)	δ^{30}Si (‰)	^{26}Al/^{27}Al
M7-A	59 ± 3	996 ± 37	1010 ± 46	
M7-B	178 ± 20	1149 ± 70	826 ± 79	
M7-C	152 ± 5	800 ± 15	1367 ± 21	0.015 ± 0.004
M7-D	109 ± 2	1082 ± 12	1207 ± 16	0.122 ± 0.012
Grain	**δ^{33}S (‰)**	**δ^{34}S (‰)**	**δ^{42}Ca (‰)**	**δ^{44}Ca (‰)**
M7-A	-72 ± 130	-115 ± 55		
M7-B	-284 ± 207	7 ± 106		
M7-C	-624 ± 84	-642 ± 35	-213 ± 280	1854 ± 307
M7-D	-609 ± 61	-478 ± 30	-142 ± 240	18160 ± 530

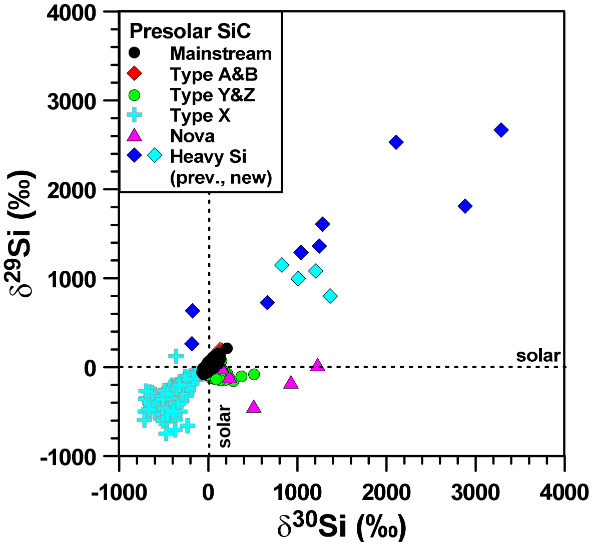

Figure 1. Si-isotopic compositions of presolar SiC.

It was argued before that SiC grains with heavy Si most likely formed in SN ejecta [3,5]. Our finding of now extinct ^{44}Ti in these grains finally proofs this scenario. The inferred ^{44}Ti/^{48}Ti ratios are within the range observed for X grains [9,10]. The grains with heavy Si, however, do not follow the observed negative correlation between δ^{29}Si and ^{44}Ti/^{48}Ti in X grains. Also the ^{26}Al/^{27}Al ratios of grains C and D are within the range typically observed for X grains [1].

Our measurements confirm that ^{32}S enrichments are a common feature of SiC grains with heavy Si. The S-isotopic signatures (Fig. 2) clearly point to significant contributions of matter from the Si/S zone, which has low $^{33}S/^{32}S$ and $^{34}S/^{32}S$ ratios (Fig. 4). Since this zone is also very rich in ^{28}Si it is not possible to simultaneously account for heavy Si, which requires significant contributions from the O/Si…O/C zones (Fig. 4), and light S in ad-hoc SN mixing calculations (Fig. 3). We note that the observed negative correlation between $\delta^{30}Si$ and $\delta^{34}S$ should be taken with care since grains A and B have 5-10x higher S concentrations than grains C and D and their S isotope data might be strongly compromised by S contamination.

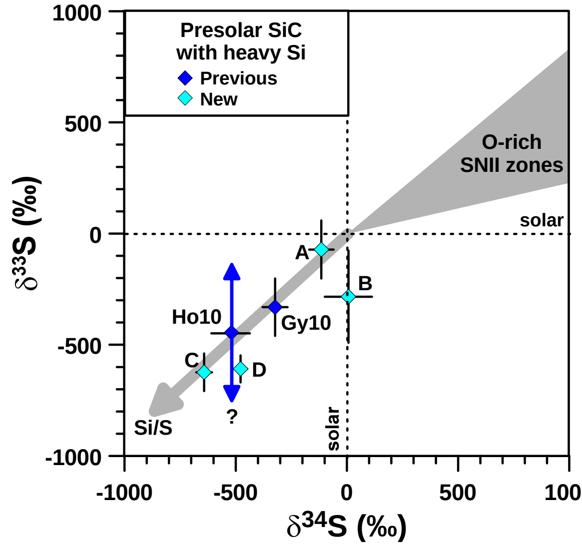

Figure 2. S-isotopic compositions of SiC grains with heavy Si. Grains A…D: this work; Ho10: [5], no $\delta^{33}S$ data; Gy10: [6].

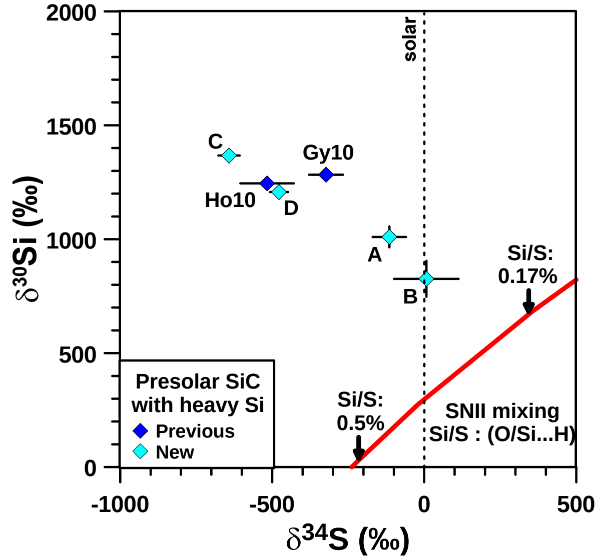

Figure 3. $\delta^{30}Si$ vs. $\delta^{34}S$ in SiC with heavy Si. The red line represents a prediction from a typical mixing scenario in a 15 $M_{\odot}$ SNII [11] that results in heavy Si.

Hoppe et al. [5] argued for preferential trapping of S from the Si/S zone due to efficient CaS formation in the Si/S zone which was later incorporated into the growing SiC grains. However, this scenario can be ruled out for grain D. Its Ca/S ratio of 0.07 is incompatible with incorporation of S as CaS. This remains true even if we consider S contamination since this is limited to ~50% in view of the observed S isotope anomalies. An alternative possibility might be incorporation of SiS from the Si/S zone. The SiS molecule is indeed an important constituent in SNII ejecta [12]. What is clearly needed are sophisticated mixing models that consider the molecule chemistry in SN ejecta. Future work should also focus on the S isotope systematics of X grains which incorporated more matter from the Si/S zone than the grains with heavy Si.

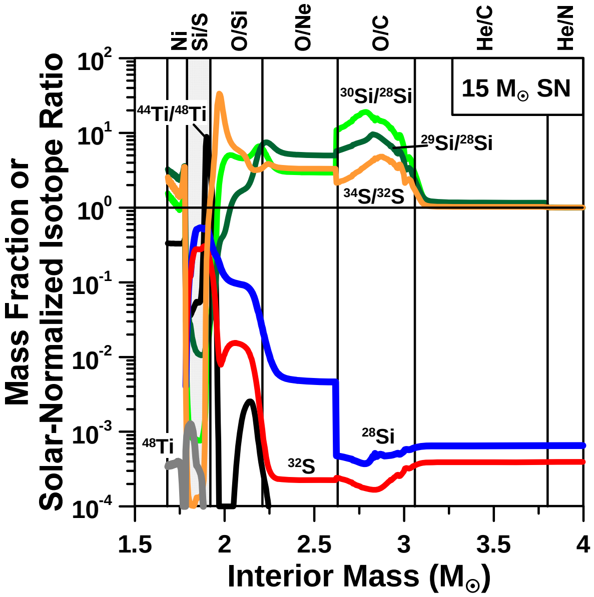

Figure 4. Profiles of selected isotopes and solar-normalized isotope ratios in a 15 $M_{\odot}$ SNII [11].

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References: [1] Zinner E. (2007) in *Treatise on Geochemistry, Vol. 1* (eds. A. Davis et al.), 1. [2] Amari S. et al. (1999) *ApJ*, 517, L59. [3] Croat T. K. & Stadermann F. J. (2010) *AJ*, 139, 2159. [4] Zinner E. et al. (2010) *LPSC*, 41, #1359. [5] Hoppe P. et al. (2010) *ApJ*, 719, 1370. [6] Gyngard F. et al. (2010) *MAPS*, 45, A72. [7] Fujiya W. et al. (2011) this meeting. [8] Gröner E. & Hoppe P. (2006) *Appl. Surf. Sci.*, 252, 7148. [9] Besmehn A. & Hoppe P. (2003) *GCA*, 67, 4693. [10] Lin Y. et al. (2010) *ApJ*, 709, 1157. [11] Rauscher T. et al. (2002) *ApJ*, 576, 323. [12] Cherchneff I. & Lilly S. (2008) *ApJ*, 683, L123.