PRESOLAR SIC GRAINS FROM SUPERNOVAE WITH UNUSUAL SILICON- AND SULFUR-ISOTOPIC COMPOSITIONS. P. Hoppe¹, E. Gröner¹, J. Huth¹, and S. Amari², ¹Max Planck Institute for Chemistry, Particle Chemistry Department, 55020 Mainz, Germany (peter.hoppe@mpic.de), ²Laboratory for Space Sciences and the Physics Department, Washington University, St. Louis, MO 63130, USA.

Introduction: Presolar grains are found in small quantities in primitive Solar System materials [1]. An important presolar mineral is SiC. Most of these grains originate from 1-3 M_{\odot} AGB stars. A small fraction also formed in nova and supernova (SN) explosions. To date most of the available isotope data are for umsized grains. However, submicrometer-sized grains represent most of the mass of presolar SiC, e.g., ~75 % in Murchison [2]. A comprehensive characterization of submicrometer-sized presolar SiC is thus important to get a complete picture of SiC formation. First NanoSIMS studies of submicrometer-sized SiC grains revealed much higher abundances of the rare and highly interesting Z grains compared to the larger grains [3,4] and identified a grain with unusual isotopic compositions [5].

Here, we report on extended C and Si isotope studies of individual SiC grains from the Murchsion separate KJA (~300 nm) [2], complemented by a N and S isotope measurement on one grain. The major goal of this study is the search for grains with unusual isotopic compositions. Such rare grains are naturally of great interest because they permit to get insights into specific aspects of stellar nucleosynthesis and evolution.

Experimental: Thousands of KJA grains were dispersed on a clean gold foil. The C- and Si-isotopic measurements were done in a fully automated imaging mode with the NanoSIMS at Max Planck Institute for Chemistry [6]. For this purpose a focussed Cs^+ beam (100 nm, 1 pA) was rastered over 164 areas, each 30 x 30 μ m² in size. Quick overview images of ¹²C, ¹³C, ²⁸Si, ²⁹Si, and ³⁰Si were acquired in multi-collection to identify SiC grains which were then measured for C and Si isotopes individually (raster size: 2x grain diameter). Four grains with special Si-isotopic signatures were subsequently re-measured with high spatial resolution in the image mode (2 x 2 μ m²). One of these grains (grain *B* below) was also measured for ${}^{15}N/{}^{14}N$ and ${}^{34}S/{}^{32}S$ by analyzing ${}^{12}C^{14}N$, ${}^{12}C^{15}N$, ${}^{28}Si$, ${}^{32}S$, and ³⁴S in multi-collection.

Results and Discussion: The automated particle recognition identified some 615 presolar SiC grains on the KJA mount. Among them are ~86 % mainstream (MS) grains, ~4 % AB grains, ~8 % YZ grains, ~1.5 % X grains, and ~1 % grains which cannot be classified into one of these groups. These numbers are roughly compatible with what has been observed for slightly

larger grains from Indarch [3] and Murchison KJB [4]. The histogram of ${}^{12}C/{}^{13}C$ ratios (Fig. 1) shows not only the well-known peak around ${}^{12}C/{}^{13}C = 60$ but a second, smaller peak around 20. However, it is possible that this peak results from multi-grain assemblages containing one AB and one or two MS grains rather than being a unique feature of small SiC grains.



Figure 1. Histograms of ${}^{12}C/{}^{13}C$ ratios in presolar SiC from Murchison. Data sources: [4] (KJB) and this work (KJA).

Figure 2 shows the Si-isotopic compositions of the KJA grains. Most of the grains show well-known isotope characteristics. Three grains, labelled *A-C*, however, need further attention. Grain *A* plots left to the SiC MS line, with a moderate enrichment in ²⁹Si and moderate depletion in ³⁰Si, and ¹²C/¹³C = 368. A similar characteristics, though with more extreme ²⁹Si enrichment, was recently observed for a KJB grain [5]. The multi-element isotope data of the KJB grain are well explained by an origin in a 15 M_{\odot} SNII, with a relatively large contribution from the O/Ne zone and modified ²⁹Si yield, and the same scenario is suggested for grain *A* of this study.

Grain *B* has very high enrichments in ²⁹Si and ³⁰Si by factors of 2.4 and 2.3, respectively, ${}^{12}C/{}^{13}C = 387$, and ${}^{14}N/{}^{15}N = 43$. Two SiC grains (one within graphite) with similar Si-isotopic characteristics were observed by [7,8]. Grain *B* has a relatively high S content (wt. permil) with $\delta^{34}S = -520 \pm 90$ ‰. The most likely source of grain *B* is a SNII. The C- and Si-isotopic

signatures can be well reproduced along with having C/O ~1 in the ejecta if matter from the O/Si, O/Ne, O/C, He/C, He/N, and H zones in the 15 M_o SNII model of [9] is mixed in appropriate proportions and if the ²⁹Si yield in the O/Si and O/Ne zones is increased by a factor of 2 [5,10]. However, the predicted ${}^{14}N/{}^{15}N$ ratio of this mixture is about a factor of 2 and the 34 S/ 32 S ratio a factor of 4 too high. Especially the low $^{34}S/^{32}S$ ratio poses a serious problem in the context of current SNII models in which ³⁴S is highly enriched in the O-rich zones (Fig. 3). Only in the Si/S zone it is strongly depleted but significant admixture of matter from this zone would decrease predicted ²⁹Si and ³⁰Si enrichments considerably. It is possible to achieve a satisfactory fit to the grain's Si and S isotope data only if the ³⁴S abundance in the O/Si zone would be ~100x lower. The same basic problem is encountered if we consider a 25 M_o SNII.



Figure 2. Si-isotopic compositions of presolar SiC grains from Murchison separate KJA. Grains *A*, *B*, and *C* have unusual isotopic signatures and are discussed in the text.

An interesting possibility to account for the observed Si and S isotope characteristics may be the following: Molecule formation occurs early in SNII ejecta and S-bearing molecules, e.g., SiS, are important constituents of SN ejecta [11]. Because Si, S, and Ca are very abundant in the Si/S zone, SiS and CaS may already form before thorough mixing with matter from overlaying layers and SiC dust formation occur. SiS and CaS play important roles in the pathway of SiC formation and CaS is known to form solid solutions with SiC [12]. In this way, comparably large amounts of S from the Si/S zone may have been incorporated as CaS into the condensing SiC grains. Clearly, more detailed work on the S chemistry in SNII ejecta is needed to follow-up on this idea. Grain *C* exhibits even higher enrichments in ²⁹Si and ³⁰Si than grain *B* with δ^{29} Si = 1800 ‰ and δ^{30} Si = 2900 ‰ and it has a lower-than-solar ¹²C/¹³C of 79. The Si-isotopic signature can be quantitatively explained by SNII mixtures; however, a satisfactory fit is achieved only for C/O < 1 and predicted ¹²C/¹³C ratios are much higher (> 10x) than observed, the result of large contributions from the O/C zone. Unfortunately, no S isotope data are available for this grain.

The study of KJA grains has shown that a small, but important fraction of submicrometer-sized SiC grains has unusual isotope characteristics. In particular, there seems to be a recognisable sub-population of SN grains with isotopically heavy Si among the smallest SiC grains. With these grains the abundance of SN grains among the KJA grains is about a factor of 2 higher than that of µm-sized SiC grains. The observed Si and S isotope characteristics of two grains studied here add to the complexity of SN grains and represent challenges for future SNII models.



Figure 3. Profiles of 12 C, 28 Si, 32 S, 29,30 Si/ 28 Si, and 34 S/ 32 S in the interior of a 15 M $_{\odot}$ SNII [8].

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