

PROBING THE EARLY SOLAR NEBULA WITH METEORITIC SILICON NITRIDE. J. Leitner¹, C. Vollmer², A. J. King³, P. F. Schofield³, J. F. W. Mosselmans⁴, and P. Hoppe¹, ¹Max Planck Institute for Chemistry, Hahn-Meitner-Weg 1, 55128 Mainz, Germany (jan.leitner@mpic.de), ²Universität Münster, Institut für Mineralogie, Corrensstr. 24, 48149 Münster, Germany, ³Earth Sciences, Natural History Museum, Cromwell Road, London SW7 5BD, UK, ⁴Diamond Light Source Ltd, Harwell Science and Innovation Campus, Chilton, OX11 0QX, UK.

Introduction: Silicon nitride (Si_3N_4) is a rare component in various chondritic meteorites [e.g., 1–3]. Besides a presolar population (i.e., these grains come from stars other than the Sun and were incorporated into the forming Solar System bodies ~4.6 Ga ago [e.g., 4]), Si_3N_4 of Solar System origin has been identified in several enstatite (ECs) and ordinary chondrites (OCs) [1,2,5]. We found evidence that the silicon nitrides in metal-sulfide-assemblages in several ECs of petrologic types 3–4 formed in the solar nebula, and not by exsolution processes on the meteorite parent body [6]. Thus, thorough investigation of these Si_3N_4 grains could reveal more detailed information on the formation conditions of the metal-sulfide-hosts, and the physical and chemical properties of the part of the solar nebula from which they originate.

Samples & Experimental: Silicon nitride grains were identified by SEM-EDS element mapping in thin sections of the ECs Pecora Escarpment (PCA) 91020 (EL3) and Indarch (EH4), as well as the OC Mezö-Madaras (L3.7). Suitable grains were selected for C- & N-isotopic analysis with the NanoSIMS 50 at the MPI for Chemistry. A ~100 nm Cs^+ primary ion beam (~1 pA) was rastered over selected sample areas, and secondary ion images of $^{12,13}\text{C}^-$, $^{12}\text{C}^{14}\text{N}^-$, $^{12}\text{C}^{15}\text{N}^-$, and $^{28}\text{Si}^-$ were recorded. In a second session, the S-isotopic compositions and S-contents of several grains from PCA 91020 and Indarch were determined (Fig. 1), with $^{28}\text{Si}^-$ and $^{32,33,34}\text{S}^-$ measured in multi-collection. S/Si ratios were calculated from $^{32}\text{S}^-/^{28}\text{Si}^-$ using a sensitivity factor $\epsilon(\text{S}^-)/\epsilon(\text{Si}^-)$ of 3 [7]. S concentrations were then estimated by assuming for each nitride a stoichiometric composition.

Two large Si_3N_4 -grains (several μm in size) from PCA 91020 previously studied by transmission electron microscopy (TEM), containing low concentrations of sulfur (~0.3–2 at%) [6] were selected for S-XANES analysis on beamline I18 at Diamond Light Source, UK [8]. With a beamsize of $1.7 \times 1.7 \mu\text{m}^2$ and a Si-drift Vortex detector, XRF maps were collected from the sections at 2.6 keV to identify pixels with high S and Si from which XANES spectra could be acquired. Both TEM lamellae were studied afterwards with a ThermoFisher Titan “Themis” G3 (300 kV) equipped with a four-quadrant silicon-drift EDS detector (“SuperX” technology). Drift-corrected STEM-EDS spectrum

image maps of both grains were recorded to search for nanosulfide inclusions.

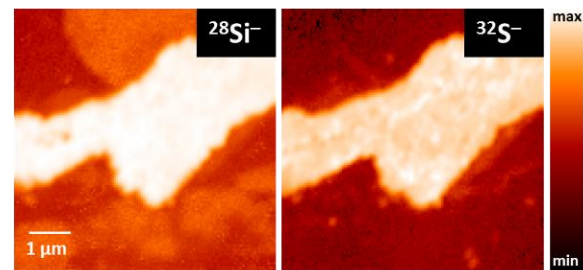


Figure 1. Secondary ion (SI) images of $^{28}\text{Si}^-$ and $^{32}\text{S}^-$ from grain PCA-B41#2-255. The sulfur is clearly present within the Si_3N_4 showing a heterogeneous distribution. The host metal shows only a low background level of $^{32}\text{S}^-$, together with few sub- μm -sized S-bearing grains.

Results & Discussion: *Mezö-Madaras.* We identified 24 Si_3N_4 grains by SEM-EDS investigation in one metal-sulfide-inclusion. The largest grain is $830 \times 360 \text{ nm}$ in size, while most of the nitrides lie between 100 nm and 200 nm. Almost all of the grains contain detectable Cr, with several of the larger nitrides showing resolvable subgrains in both BSE and EDS maps, suggesting they are Si_3N_4 -CrN-intergrowths instead of Cr-bearing silicon nitrides. The C- and N-isotopic compositions of six grains were subsequently measured by NanoSIMS. The $\delta^{15}\text{N}$ -values range from $-236 \pm 147 \text{ ‰}$ to $10 \pm 25 \text{ ‰}$, with a weighted average of $-27 \pm 14 \text{ ‰}$; C-isotopic compositions are close to solar. Statistics are still very limited, and statistical errors comparably large, but the nitrides appear to have N-isotopic compositions similar to the EC- Si_3N_4 , indicating a common origin of OC- and EC- Si_3N_4 .

Enstatite Chondrites. We obtained C- and N-isotopic data for 14 grains from PCA 91020 (d~1–5 μm) and 10 grains from Indarch (d~0.4–10 μm) (Fig. 2). The PCA grains have $\delta^{15}\text{N}$ -values ranging from $-81 \pm 5 \text{ ‰}$ to $-16 \pm 24 \text{ ‰}$, with an average of $-67 \pm 2 \text{ ‰}$, and the Indarch grains are between $-56 \pm 4 \text{ ‰}$ and $8 \pm 3 \text{ ‰}$, with an average $\delta^{15}\text{N}$ of $-43 \pm 1 \text{ ‰}$. The C-isotopic compositions are generally close to the terrestrial value, with average $\delta^{13}\text{C}$ of $-16 \pm 2 \text{ ‰}$ (PCA) and $5 \pm 1 \text{ ‰}$ (Indarch). These findings agree well with previous results for 288 silicon nitrides from a set of ECs with a $\delta^{15}\text{N}_{\text{avg}}$ of $-60 \pm 1 \text{ ‰}$ and a $\delta^{13}\text{C}_{\text{avg}}$ of $4 \pm 1 \text{ ‰}$ [6].

NanoSIMS S-investigation. S-isotopic compositions and S-abundances were determined for 63 Si_3N_4 grains from PCA 91020 and 6 grains from Indarch. For PCA, $\delta^{33}\text{S}$ ranges from -84 ± 46 ‰ to 43 ± 21 ‰ (average of -5 ± 4 ‰), and $\delta^{34}\text{S}$ -values lie between -40 ± 14 ‰ and 35 ± 14 ‰ (average of 2 ± 4 ‰). S/Si-ratios range from 0.003 to 0.09, corresponding to estimated sulfur concentrations of 0.14–4 at%. For the six grains from Indarch, we obtained S-isotopic compositions similarly close to the terrestrial values (average $\delta^{33,34}\text{S}$ -values of -9 ± 4 ‰ and 1 ± 4 ‰, respectively). The S/Si-ratios range from 0.008 to 0.07, and estimated sulfur abundances lie between 0.4 and 3 at%. Sulfur is clearly present in all the grains, while the host metal shows significantly lower $^{32}\text{S}^-$ -signals (Fig. 1). Moreover, no gradients in the S-distribution indicative of diffusion, or S-bearing veins crossing grain boundaries were visible. Thus, the S must have been present in the Si_3N_4 when it was incorporated into the meteorites.

S K-edge XANES and TEM results. All XANES spectra represent “bulk” information on the sulfur in the two nitride grains. For PCA-B41-01, all spectra are similar in structure, suggesting that the S is in the same chemical state and environment throughout the grain. They are similar to S XANES spectra from 1:1 transition metal sulfides with a sharp ‘pre-edge’ feature at ~ 2470.2 eV and a broad feature at 2477 eV and 2482 eV [9,10], in which the S is considered to be in the 2^- state. There are no other cations spatially associated with the S, and it is likely that the Si is structurally incorporated into the Si_3N_4 as S^{2-} . XANES spectra from PCA-E21-F1-01 are more complex than those from PCA-B41-01, with a diminished pre-edge feature at 2470.3 eV, and three maxima at ~ 2473.2 , 2477.8 and 2482.0 eV. This suggests that the S is in mixed oxidation states, with structurally incorporated S^{2-} in addition to oxidized S species. The peaks at ~ 2477.8 and 2482 eV in the spectra may be associated with S^{4+} and S^{6+} , however when considered with the peak at ~ 2473.2 eV they may reflect the presence of bisulphite- or thiosulphate-like S species [9,11]. S^{2-} remains the dominant species, with the S^{4+} and S^{6+} also structurally incorporated into the Si_3N_4 , potentially with traces of O. Subsequent STEM-EDS mapping showed no nano-sulfide inclusions within the two silicon nitrides, supporting our interpretation of structurally bound S within the Si_3N_4 . Together with the results of the NanoSIMS-investigations, this strongly suggests that the sulfur was not introduced into the nitrides after they were incorporated in their host phases, but is *indigenous* to the Si_3N_4 . There might have been a sulfidization event while the nitrides still resided in the early solar nebula; a similar scenario was recently proposed

for S-bearing refractory metal nuggets (RMNs) [12]. Alternatively, S could have been incorporated during nitride formation. Under reducing (i.e., inner Solar System) conditions, SiS has been found to become the dominant gaseous species instead of H_2S [13], a viable source for S in correlation with Si. Thus, our findings support an inner Solar System origin of the Si_3N_4 , with the S directly inherited from the solar nebula.

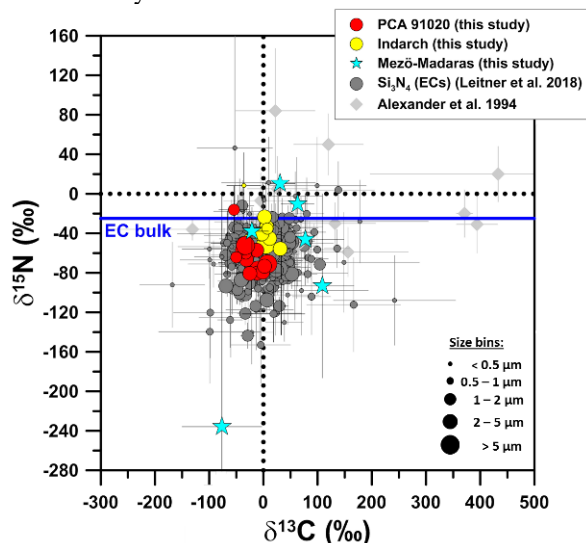


Figure 2. C- & N-isotopic compositions of 24 Si_3N_4 grains from PCA 91020 and Indarch, together with 6 grains from Mezö-Madaras. Reference data from [1] and [6] (2 grains with $\delta^{13}\text{C} > 500$ ‰ are not shown) are displayed in grey. Errors are 1σ . Terrestrial values are marked by the black dotted lines, and the solid blue line denotes the average EC bulk N-isotopic composition. The star symbols are not scaled according to the size bins.

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