

INVESTIGATION OF NITRIDES IN CARBONACEOUS CHONDRITES: A WINDOW TO EARLY SOLAR NEBULA PROCESSES? J. Leitner¹, C. Vollmer², D. Harries³, J. Kodolányi¹, U. Ott¹, and P. Hoppe¹, Max 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, ³Institute of Geoscience, Friedrich Schiller University Jena, Carl-Zeiss-Promenade 10, 07745 Jena, Germany.

Introduction: Chondritic meteorites contain small quantities of various nitrides (Si_3N_4 , TiN , CrN) and sinoite ($\text{Si}_2\text{N}_2\text{O}$). A very rare population (abundances of tens of parts per billion) of *presolar* Si_3N_4 has been identified in the matrix of several chondrites. These grains formed in the ejecta of supernova explosions before the formation of the Sun and the Solar System, and are characterized by highly anomalous N- and Si-isotopic compositions [e.g., 1]. Another Si_3N_4 population, of Solar System origin, has been found in enstatite chondrites (ECs) [2–4] and several ordinary chondrites (OCs) [3, 5]. Osbornite (TiN) was detected in the metal-rich chondrites Allan Hills (ALH) 85085 (CH3) and Isheyevo (CH/CB) [6–9], and two recent studies reported the occurrence of CrN (carlsbergite) in P- and Cr-rich Fe,Ni-sulfides and metal grains in several CM chondrites [10,11]. For the CrN in CM chondrites, formation in the solar nebula has been inferred, and a recent investigation of Si-nitrides from a set of ECs found similar evidence for a nebular origin [4]. Thus, a comprehensive investigation of nitrides in chondritic meteorites could provide insights into the different nitrogen reservoirs in the chondrite forming regions (if a nebular origin of such nitrides can be ascertained), and would allow further conclusions about the formation conditions for the nitride hosts. Here, we report the discovery of Si_3N_4 , CrN , and potentially sinoite in metal-sulfide grains from several carbonaceous chondrites.

Samples & Experimental: We investigated metal-sulfide inclusions in the carbonaceous chondrites Leoville (CV3_{red}), Coolidge (C4-ung.), Acfer 182 (CH3), ALH 85085 (CH3), and Isheyevo (CH/CB_b). All samples were characterized by backscatter electron (BSE) imaging and EDS mapping with a LEO 1530 FE-SEM at the Max Planck Institute for Chemistry (MPIC), equipped with an Oxford X-Max 80 SDD detector. The C- and N-isotopic compositions of suitable N-bearing grains were then measured with a NanoSIMS ion probe at the MPIC, by rastering a ~ 100 nm Cs^+ primary ion beam (~ 1 pA) over selected sample areas. 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 multi-collection mode. C- and N-isotopic compositions are reported as δ -values (in ‰) relative to synthetic SiC - and Si_3N_4 -standards.

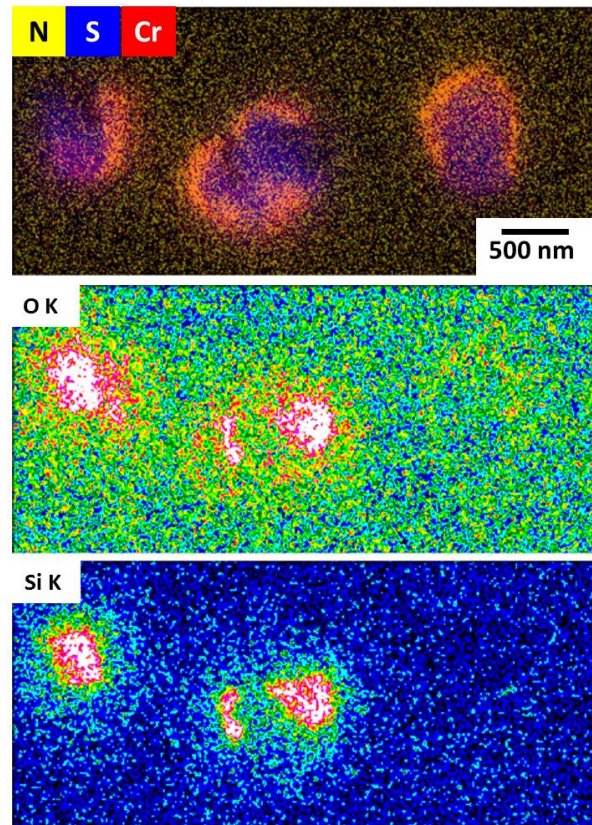


Figure 1. RGB-map (top) showing the distribution of N (yellow), S (blue), and Cr (red) for three CrN -bearing sulfide inclusions from Acfer 182, together with elemental distribution maps of O (center) and Si (bottom).

Results: In each thin section, Si_3N_4 , CrN , or a combination of both nitrides were found. C- and N-isotopic data have been obtained so far for grains from Leoville, Acfer 182, ALH 85085, and Isheyevo.

Leoville. Two large Fe,Ni metal grains (~ 1.5 mm \times 1.1 mm and ~ 1.5 mm \times 1 mm in size, respectively) located within a chondrule were found to host several hundred Si_3N_4 grains (up to several μm in size), as well as small (50–500 nm) Cr-V-nitrides. Several Si-nitrides contain (Cr,V)N-subgrains. The N-isotopic compositions of 16 Si-nitrides range from $\delta^{15}\text{N} = -8 \pm 23$ ‰ to $+277 \pm 35$ ‰, and two CrN grains have $\delta^{15}\text{N}$ of -4 ± 31 ‰ and $+36 \pm 15$ ‰, respectively.

Coolidge. Several metal grains show abundant small Si-rich inclusions. Detailed investigation of three metal grains revealed N-rich sub-areas in 27 SiO_2 in-

clusions, consisting either of Si_3N_4 or $\text{Si}_2\text{N}_2\text{O}$. Sizes of the N-rich inclusions range from ~50 to 500 nm.

CH chondrites & Isheyevo. In Acfer 182 and ALH 85085, 43 and 25 CrN-bearing Fe-Cr-sulfide inclusions, respectively, were found in four Fe,Ni metal grains (two host grains in Acfer 182 and two in ALH 85085). In Isheyevo, we identified eight Si_3N_4 grains, as well as ten CrN grains, located in two different Fe,Ni grains. The CrN in Acfer 182 occurs as shells and partial shell-like structures around Cr-bearing Fe,Ni sulfides, sometimes intergrown with SiO_2 (Fig.1). In contrast, the sulfide inclusions in ALH 85085 are correlated with distinct CrN grains (39 in total) with sizes of 50–250 nm. N-isotopic compositions of the CrN grains in the three metal-rich chondrites range from $\delta^{15}\text{N} = +48 \pm 170\%$ to $+176 \pm 374\%$. The Si_3N_4 from Isheyevo has significantly lighter nitrogen, with $(-175 \pm 85\%) \leq \delta^{15}\text{N} \leq (+74 \pm 60\%)$ and is located in a Si-bearing (~3 wt.%) metal grain.

Discussion: Various processes might explain the formation of meteoritic nitride minerals, e.g., precipitation from N-saturated metal grains suspended in an N-rich gas [e.g., 10], or condensation under non-equilibrium conditions, e.g. in the wake of planetesimal collisions [4]. Previous studies [4,10] found evidence for a nebular origin of the CrN in CM sulfides and the Si_3N_4 in ECs. Furthermore, the average N-isotopic compositions of the nitrides from the CMs and the ECs are significantly different ($+50\%$ and -60% , Fig. 2), which might be explained by origins from isotopically distinct nebular reservoirs. The Si_3N_4 grains in Leoville have heavier N-isotopic compositions ($\delta^{15}\text{N}_{\text{avg}} = 31 \pm 2\%$) than the EC-Si-nitrides. Moreover, the estimated N abundances in the host grains are higher than 1,000 ppm, exceeding the maximum amount of N that can be stored in Fe,Ni metal in solid solution. Thus, exsolution of the nitrides under parent body conditions can be excluded, and we propose formation in the solar nebular instead, as suggested by [4] and [10]. The Si-nitrides found in Isheyevo have an N-isotopic range comparable to the EC Si_3N_4 (Fig. 2), although for the CH and CB chondrites an outer Solar System origin is suggested [e.g., 12]. Interestingly, the metal host has a Si content comparable to EH metal, and contains schreibersite $[(\text{Fe},\text{Ni})_3\text{P}]$ and niningerite $[(\text{Mg},\text{Mn})\text{S}]$, which frequently occur in ECs. The CrN in Isheyevo and the two CH chondrites studied here, however, contain isotopically heavy N (Fig. 2), with $\delta^{15}\text{N}$ in the same range as observed for matrix clasts, metal grains, and bulk N in CH and CB chondrites [e.g., 13 and refs. therein]. This could indicate that most of the N in the CH/CBs originated from an isotopically heavy (presumably outer Solar System) reservoir, while Isheyevo

contains in addition N from small amounts of EC-like material (of potential inner Solar System origin). The different N-isotopic compositions of the nitrides could be explained by mixing isotopically light N from the protosolar nebula [14] with an ^{15}N -rich component from the outer Solar System. The sequence EC-(OC-) CV&CM-CH&CB (with increasing $\delta^{15}\text{N}$) could then indicate increasing amounts of outer Solar System N in the respective reservoirs, reflecting different heliocentric distances of the formation regions [14]. Investigation of nitrides in other carbonaceous chondrite groups would allow to test and refine this assumption.

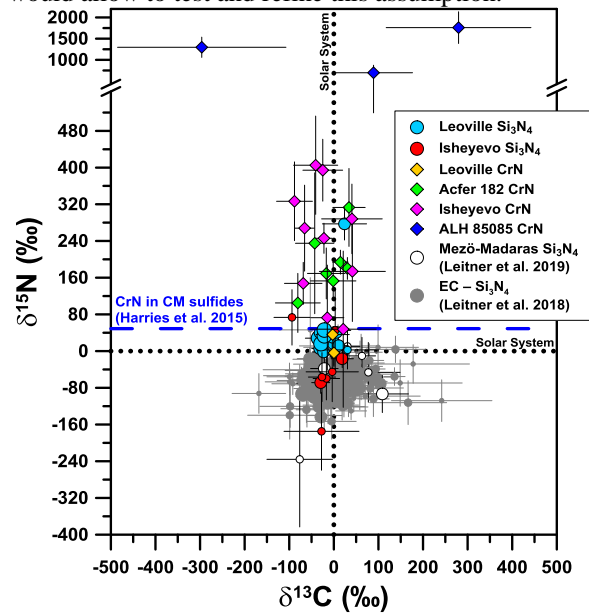


Figure 2. C-N-isotope plot for Si_3N_4 and CrN from the meteorites of this study, together with literature data for Si-nitride from ECs [4] and the OC Mezö-Madaras [5]. The average N-isotopic composition of CrN from CM chondrites [10] is marked by the blue dashed line.

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