A STUDY OF CHROMIUM AND SILICON NITRIDES IN CARBONACEOUS CHONDRITES. J. Leitner[1], C. Vollmer[2], D. Harries[3], J. Kodolányi[1], U. Ott[1], and P. Hoppe[1], Max Planck Institute for Chemistry, Hahn-Meitner-Weg 1, 55128 Mainz, Germany (jan.leitner@mpic.de), [2]Universität Münster, Institut für Mineralogie, Corrensstr. 24, 48149 Münster, Germany, [3]Institute of Geoscience, Friedrich Schiller University Jena, Carl-Zeiss-Promenade 10, 07745 Jena, Germany.

Introduction: Various nitrides (Si_3N_4, TiN, CrN) and sinoite (Si_2N_2O) have been found in small amounts in chondritic meteorites. A very rare population (abundances of tens of ppb) of *presolar* Si_3N_4 is present in the matrix of several chondrites, characterized by highly anomalous N- and Si-isotopic compositions [e.g, 1]. Si_3N_4 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 studies reported the occurrence of CrN (carlsbergite) in P- and Cr-rich Fe,Ni-sulfides and metal grains in several CM chondrites [10,11]. Formation in the solar nebula has been inferred for both the CrN in CM chondrites [10] and the Si-nitrides from a set of ECs [4]. A comprehensive investigation of Solar System nitrides has the potential to provide insights into the different nitrogen reservoirs in the chondrite forming regions, and might allow further conclusions about the formation conditions for the nitride hosts. Here, we report on our ongoing investigation of Si_3N_4 and CrN in metal-sulfide grains in a set of carbonaceous chondrites.

Samples & Experimental: We investigated metal-sulfide inclusions in the carbonaceous chondrites Leoville ($CV3_{red}$), Vigarano ($CV3_{red}$), Coolidge (C4-ungr.), Banten (CM2), Murchison (CM2), Murray (CM2), Yamato (Y-) 791198 (CM2), Acfer 094 (C2-ungr.), Renazzo (CR2), Elephant Moraine (EET) 92161 (CR2), Queen Alexandra Range (QUE) 99177 (CR2), Northwest Africa (NWA) 530 (CR2), NWA 801 (CR2), NWA 852 (CR2), NWA 6957 (CR2), 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 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 $^{12,13}C^-$, $^{12}C^{14,15}N^-$, and $^{28}Si^-$ 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 with assumed terrestrial atmospheric isotope composition.

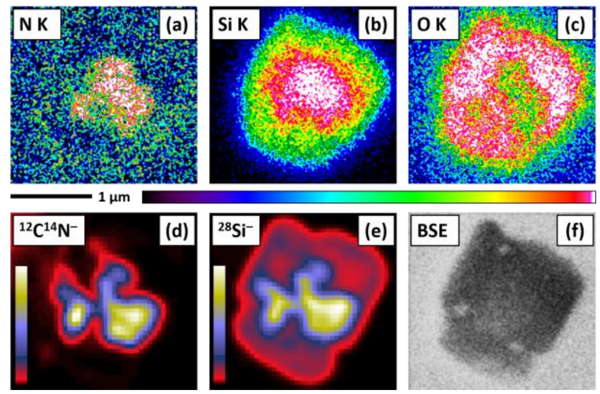

Figure 1. *EDX element distribution maps of N (a), Si (b), and O (c) for an Si_3N_4 inclusion with Si-oxide mantle from Coolidge, together with secondary ion images of $^{12}C^{14}N^-$ (d) and $^{28}Si^-$ (e), and BSE image (f) of the same area.*

Results: In each thin section, we identified Si_3N_4, CrN, or a combination of both. C- and N-isotopic data have been obtained for grains from Leoville, Coolidge Murchison, Y-791198, Acfer 094, Renazzo, QUE 99177, NWA 801, NWA 6957, Acfer 182, ALH 85085, and Isheyevo.

CV chondrites & Coolidge. Two large mm-sized Fe,Ni metal grains located within a Leoville 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 26 Si-nitrides range from $\delta^{15}N$ = –17±24 ‰ to +277±35 ‰, and four CrN grains have $\delta^{15}N$ from –12±63 ‰ to +283±247 ‰ ($\delta^{15}N_{avg}$ = +30±2 ‰ and +27±13 ‰, respectively). In Vigarano, two Fe,Ni metal inclusions (~20 µm in size) in a large Fe-sulfide grain contain several dozen Si_3N_4 grains (d ≤150 nm) enclosed in sub-µm-sized Fe-phosphates. Detailed investigation of three metal grains from Coolidge revealed N-rich sub-areas consisting of Si_3N_4 (d~50 to 500 nm) located in 34 Si-oxide inclusions (Fig. 1). The average N isotope composition of six grains is $\delta^{15}N_{avg}$ = +31±6 ‰.

CH chondrites & Isheyevo. All three meteorite sections contain nitride-bearing metal grains. CrN and (Cr,V)N grains occur as shells and partial shell-like structures around Cr-bearing Fe,Ni sulfides, sometimes intergrown with Si-oxide, as well as distinct grains in the metal host, with sizes between 50 and 500 nm. For Acfer 182 and Isheyevo, the N-isotopic compositions range from +47±170 ‰ to 405±170 ‰, with $\delta^{15}N_{avg}$ of +144±7 ‰ and +243±21 ‰, respectively. The Cr nitrides from ALH 85085 contain significantly heavier N, with $\delta^{15}N_{avg}$ = +1476±54 ‰. The Si_3N_4 from Isheyevo, in contrast, has significantly lighter N, with an average $\delta^{15}N$ of –37±13 ‰ (Fig. 2), and is located in an Si-bearing (~3 wt.%) metal grain.

CR chondrites. We identified >200 CrN grains in 26 metal hosts from 7 meteorites. Grain sizes and morphologies are similar to CH-CB CrN. Average N-isotopes for 4 CRs range from $\delta^{15}N_{avg}$ = +89±21 ‰ (NWA 801) to +186±15 ‰ (QUE 99177) (Fig. 2).

CM chondrites & Acfer 094. The 52 CrN grains from Acfer 094 metal are comparably small (d ≤250 nm), often associated with sub-µm-sized Si-oxide spherules. Four grains were large enough for isotopic analysis ($\delta^{15}N_{avg}$ = +14±7 ‰). A P-Cr-bearing sulfide (PCS) in Y-791198 contained several CrN grains; and in three metal grains from Banten, Murchison and Murray, 29 CrN inclusions have been identified. The Murchison and Y-791198 CrN have $\delta^{15}N_{avg}$ = +42±8 ‰ and +18±7 ‰, respectively.

Discussion: We observe significant differences between the average N-isotopic compositions of the nitrides from different chondrite groups (Fig. 2). The Si_3N_4 in Leoville and Coolidge have heavier N-isotopic compositions ($\delta^{15}N_{avg}$ ~ +30‰) than the EC-Si-nitrides, while the Isheyevo-Si_3N_4 is isotopically light, comparable to those from the ECs. (Fig. 2). This observation appears to be at odds with the idea that the different N-isotopic compositions could be explained by mixing isotopically light N from the protosolar nebula with an ^{15}N-rich component from the outer Solar System, reflecting different heliocentric distances of the formation regions [12], since for the CH and CB chondrites an outer Solar System origin was suggested [e.g., 13]. However, the Isheyevo CrN is isotopically heavy, similar to the nitrides from the other two CH chondrites, with $\delta^{15}N$ in the same range as observed for matrix clasts, metal grains, and bulk N in CH and CB chondrites [e.g.,14 and refs. therein]. The Isheyevo Si_3N_4 host metal is similar to EH metal and contains schreibersite and niningerite, which frequently occur in ECs. High-Si metal and minerals typical for ECs have also been found in ALH 85085 [15]. Thus, most of the N in the CH/CBs might have originated from an isotopically heavy (outer Solar System) reservoir, but also sampled small amounts of light N, possibly delivered via outward migration of an EC-like planetesimal. The CR-CH-CB nitrides show the largest enrichments of ^{15}N in our data set (Fig. 2). The average $\delta^{15}N$ values of our CR nitrides (89 ‰–186 ‰) are compatible with the whole-rock $\delta^{15}N$ reported for CRs [16] and the N isotope anomalies of Acfer 182 and Isheyevo CrN, but CrN from ALH 85085 has significantly heavier N. The $\delta^{15}N_{avg}$ of Leoville, Murchison, Acfer 094, and Y-791198 nitrides are, within 2σ errors, comparable to the literature value for CrN from Y-791198 ($\delta^{15}N_{avg}$ = 49±15 ‰) [10]. The sequence EC-CV&CM-CR-CH&CB (with increasing $\delta^{15}N$) would then indicate increasing amounts of outer Solar System N, reflecting different heliocentric distances of the formation regions [12].

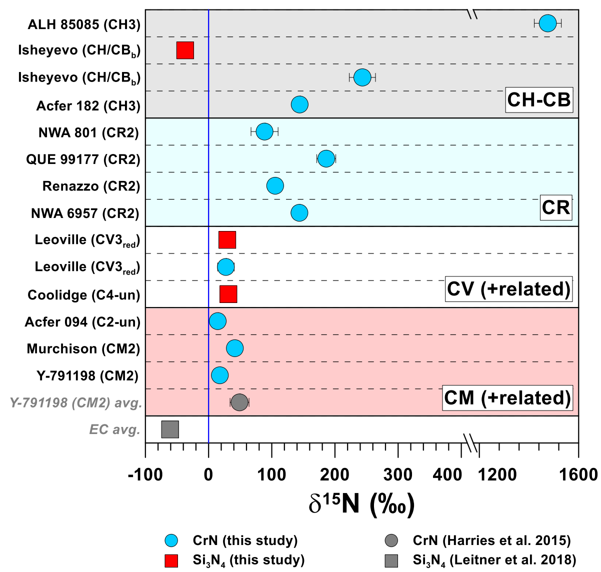

Figure 2. *N-isotope plot for Si_3N_4 and CrN from this study, together with literature data for CrN from P- and Cr-rich sulfides from Y-791198 [10] and Si_3N_4 from ECs [4].*

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