

**INVESTIGATION OF THE SILICON NITRIDE INVENTORY OF CARBONACEOUS CHONDRITES.**

J. Leitner<sup>1</sup>, C. Vollmer<sup>2</sup>, J. Kodolányi<sup>1</sup>, and P. Hoppe<sup>1</sup>, <sup>1</sup>Max Planck Institute for Chemistry, Hahn-Meitner-Weg 1, 55128 Mainz, Germany (jan.leitner@mpic.de), <sup>2</sup>University of Münster, Institute for Mineralogy, Corrensstr. 24, 48149 Münster, Germany.

**Introduction:** Silicon nitride (Si<sub>3</sub>N<sub>4</sub>) has been identified as a rare component in 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 solid bodies in the nascent Solar System [e.g., 4]), Si<sub>3</sub>N<sub>4</sub> of Solar System origin was found in several enstatite (ECs) and ordinary chondrites (OCs) [1,2,5–7]. The majority of the EC components are likely of inner Solar System origin [8], for which isotopically light N-isotopic compositions are concluded [9,10] and the N isotopes of EC-Si<sub>3</sub>N<sub>4</sub> ( $\delta^{15}\text{N}_{\text{air}} = -60 \pm 1 \text{ ‰}$ , [6]) support this conclusion. Solar System Si<sub>3</sub>N<sub>4</sub> in carbonaceous chondrites (CCs), however, has not been studied at all. There is only one record in the literature [11], where the occurrence of Si<sub>3</sub>N<sub>4</sub> in Acfer 182 (CH3) is briefly mentioned. Nitrogen-isotopic and mineralogical investigation of Si<sub>3</sub>N<sub>4</sub> grains from CCs can reveal information on their formation conditions, and thus allow conclusions about the formation regions of their meteoritic hosts. Here, we report the isotopic and mineralogical investigation of Si<sub>3</sub>N<sub>4</sub> grains from four carbonaceous chondrites.

**Samples & Experimental:** Silicon nitride grains were identified by SEM-EDS element mapping in thin sections of Leoville (CV3<sub>red</sub>), Vigarano (CV<sub>red</sub>), Coolidge (C4-un), and Isheyevo (CH/CB3). Suitable grains were then selected for isotopic analysis with the MPIC NanoSIMS 50. A ~100 nm Cs<sup>+</sup> primary ion beam (~1 pA) was rastered over selected sample areas, and secondary ion images of <sup>12,13</sup>C<sup>-</sup>, <sup>12</sup>C<sup>14</sup>N<sup>-</sup>, <sup>12</sup>C<sup>15</sup>N<sup>-</sup>, and <sup>28</sup>Si<sup>-</sup> were recorded in multi-collection. Electron-transparent lamellae from selected Si nitrides were prepared by the focused ion beam (FIB) technique at the University of Münster (Zeiss CrossBeam 340). Transmission electron microscopy (TEM) analyses were then performed on an image-corrected FEI/ThermoFisher Themis TEM (300 kV) at the University of Münster to investigate the structure and element composition of nitride grains in detail.

**Results & Discussion:** *CV chondrites & Coolidge.* Silicon nitrides appear to be less abundant in the two CVs than in the ECs studied by [6]; Leoville contains two large mm-sized Fe,Ni metal grains with several hundred Si<sub>3</sub>N<sub>4</sub> inclusions (up to several  $\mu\text{m}$  in size), occasionally containing (Cr,V)N subgrains. Carbon- & Nitrogen-isotopic data were obtained for 26 grains. The average C-isotopic composition is slightly below the terrestrial value ( $\delta^{13}\text{C}_{\text{PDB}} = -10 \pm 2 \text{ ‰}$ ), while the  $\delta^{15}\text{N}_{\text{air}}$  is  $+30 \pm 2 \text{ ‰}$ , significantly heavier than the average N-composition of EC-Si<sub>3</sub>N<sub>4</sub> [6]. In Vigarano, several dozen Si nitrides were found in two metal grains. Compared to the Leoville nitrides, the grains are small ( $d < 300 \text{ nm}$ ), and are surrounded by Fe-phosphate rims. Due to their small sizes, acquisition of N-isotopic data proved to be difficult; for two grains, we found on average  $\delta^{15}\text{N}_{\text{air}} = +65 \pm 77 \text{ ‰}$  and  $\delta^{13}\text{C}_{\text{PDB}} = -58 \pm 21 \text{ ‰}$ . Although this result appears to agree with the Leoville data, the large error does not allow an unambiguous conclusion for the N isotopes. TEM results for two Si<sub>3</sub>N<sub>4</sub> grains from Leoville show them to be nierite ( $\alpha$ -Si<sub>3</sub>N<sub>4</sub>), fractured, with several small (Cr,V)N inclusions, and carbonaceous and S-bearing material in the fractures. In Coolidge, we identified several dozen Si<sub>3</sub>N<sub>4</sub> grains in three metal host grains. Grain sizes are typically  $< 1 \mu\text{m}$ , and the nitrides feature Si-oxide rims, or are attached to (larger) Si-oxide grains. Isotopic data for 15 grains are  $\delta^{15}\text{N}_{\text{air}} = +28 \pm 5 \text{ ‰}$  and  $\delta^{13}\text{C}_{\text{PDB}} = +23 \pm 5 \text{ ‰}$ .

*Isheyevo.* Twelve Si<sub>3</sub>N<sub>4</sub> grains in two Si-bearing metal grains (~1 wt% and ~3 wt% Si) have on average  $\delta^{15}\text{N}_{\text{air}} = -76 \pm 4 \text{ ‰}$  and  $\delta^{13}\text{C}_{\text{PDB}} = 7 \pm 4 \text{ ‰}$ . Thus, the N-isotopic composition is significantly lighter than that of the Si<sub>3</sub>N<sub>4</sub> from the other three CCs and the bulk-N composition of Isheyevo [12], as well as CrN from Isheyevo [13]. Instead, the  $\delta^{15}\text{N}$  is compatible with the composition of Si<sub>3</sub>N<sub>4</sub> grains from ECs. One of the host metals occurs in association with schreibersite and niningerite, similar to the metal-sulfide nodules of ECs. Similar metal grains and mineral assemblages typical for ECs have also been found in Allan Hills (ALH) 85085 [14]. Thus, Isheyevo (and the CH chondrites) sampled small amounts of light N, possibly delivered via outward migration of an EC-like planetesimal. The N-isotopic composition of Si<sub>3</sub>N<sub>4</sub> from the CVs and Coolidge, however, suggests a formation reservoir distinct from the EC-Si<sub>3</sub>N<sub>4</sub> grains, likely at higher heliocentric distances than the EC-reservoir [9,10].

**References:** [1] Alexander C. M. O'D. et al. (1994) *Meteoritics* 29:79–84. [2] Russell S. S. et al. (1995) *Meteoritics* 30:399–404. [3] Nittler L. R. et al. (1995) *The Astrophysical Journal* 453:L25–L28. [4] Zinner E. (2014) In *Meteorites and Cosmochemical Processes* (ed. Davis A. M.). Elsevier, Amsterdam, pp. 181–213. [5] Lee M. R. et al. (1995) *Meteoritics* 30:387–398. [6] Leitner J. et al. (2018) *Geochimica et Cosmochimica Acta* 235:153–172. [7] Leitner J. et al. (2019) *LPS XL*, Abstract #2961. [8] Ebel D. S. & Alexander C. M. O'D. (2011) *Planetary & Space Science* 59:1888–1894. [9] Füri E. & Marty B. (2015) *Nature Geoscience* 8:515–522. [10] Grewal D. S. et al. (2021) *Nature Astronomy* 5:356–364. [11] Grady M. M. & Pillinger C. T. (1993) *Earth & Planetary Science Letters* 116:165–180. [12] Ivanova M. A. et al. (2008) *Meteoritics & Planetary Science* 43:915–940. [13] Leitner J. et al. (2021) *LPS XLII*, Abstract #1878. [14] Kimura M. & El Goresy A. (1989) *Meteoritics* 24:A286.