THE SILICON NITRIDE INVENTORY OF ENSTATITE CHONDRITES.
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Introduction: Enstatite chondrites (ECs) are considered to represent the best analogue material for the building blocks of the primordial Earth, due to their O-, Ca-, Ti-, Cr-, and Ni-isotopic compositions, as well as their bulk chemistry [1–5]. Their major constituents formed under highly reducing conditions and show only very minor signs of aqueous alteration [6,7], suggesting an origin in the inner solar system [8]. The whole-rock nitrogen isotopic composition of the ECs is slightly ^{15}N-depleted with $\delta^{15}N_{air}$ = –24 ‰ [e.g., 9]. Sinoite (Si_2N_2O), as well as Si- and Ti-nitrides, are generally considered as major nitrogen carriers in these meteorites, but neither their isotopic compositions nor their abundances have been well constrained so far. Only a few sinoite grains from two ECs have been studied for their N-isotopic composition [10,11]. Silicon nitride (Si_3N_4) has been investigated in acid residues from the ECs Indarch and Qingzhen [e.g., 12,13]. Apart from presolar Si_3N_4 grains, which typically show large ^{15}N-enrichments [e.g., 13], the majority of silicon nitrides in these meteorites do not show significant deviations from the terrestrial value [12], or only a small negative ^{15}N-anomaly [14]. Here, we report on results from an in-situ investigation of silicon nitride in Pecora Escarpment (PCA) 91020 (EL3), Kota-Kota (EH3), and Indarch (EH4) to determine their N-isotopic compositions in comparison with other EC constituents, and to revisit possible formation scenarios (exsolution, nebular condensation, or parent body metamorphism).

Samples & Experimental: Thin sections of PCA 91020, Kota-Kota, and Indarch were characterized by backscatter electron (BSE) mapping with a LEO 1530 FE-SEM at the Max Planck Institute for Chemistry (MPIC) in Mainz. Si_3N_4 grain candidates were identified in large-area element maps of N, O, and Si acquired with an Oxford X-Max 80 SDD EDS-detector, and their compositions were determined subsequently by quantitative EDS-measurements. Suitable grains were then selected for isotopic analysis with the MPIC NanoSIMS 50. A ~100 nm Cs^+ primary ion beam (~1 pA) was rastered over selected sample areas, and secondary ion images of $^{12,13}C^-$, $^{12}C^{14}N^-$, $^{12}C^{15}N^-$, and $^{28}Si^-$ were recorded in multi-collection.

The trace element content of one large (2×10 µm) Si_3N_4 grain from Indarch was studied with the IDLE3 TOF-SIMS at the University of Manchester, with an Au cluster liquid metal ion source (beam size ~500 nm). Transmission electron microscopy (TEM) analyses were performed on a Zeiss Libra 200FE (200 kV) at the Institute for Mineralogy at the University of Münster to investigate the structure of nitride grains.

Results & Discussion: We measured the C- and N-isotopic compositions of 268 Si_3N_4 grains from metal-sulfide assemblages from PCA 91020, Indarch, and Kota-Kota (Fig. 1). $\delta^{13}C_{PDB}$ values of individual grains range from (–168±60) ‰ to (242±113) ‰, with a weighted average δ^{13}C of (3±1) ‰, and the $\delta^{15}N_{air}$ values range from (–153±39) ‰ to (46±113) ‰, with a weighted average δ^{15}N of (–62±1) ‰. This average composition is significantly lighter than both reported

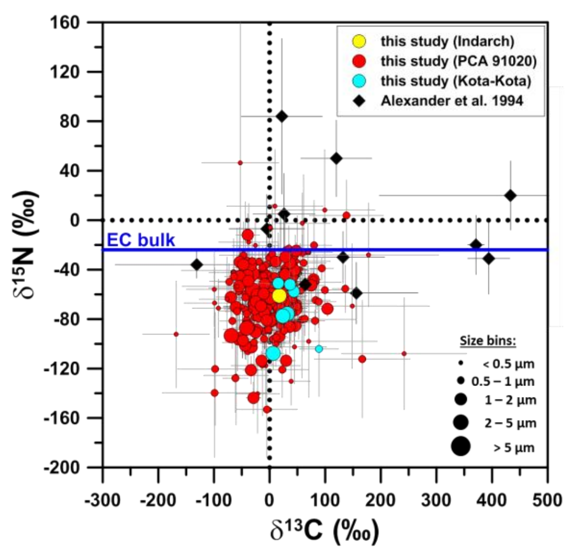

Figure 1. *C- & N-isotopic compositions of 268 Si_3N_4 grains from PCA 91020, Indarch, and Kota-Kota. Reference data are from [12] (2 grains with $\delta^{13}C$>500‰ are not shown). Errors are 1σ.*

N-isotopic compositions for bulk ECs [9,15] and the sinoite [10,11]. The N-isotopic data of Si_3N_4 from Qingzhen by [12] show no significant deviation from the terrestrial value, except for two grains with depletions in ^{15}N at the 3σ-level. The large δ^{13}C-deviations from the solar system value for several grains from [12] are attributed to adhering presolar SiC grains from the grain separate. Our data suggest a general ^{15}N-depletion for Si_3N_4 of Solar System origin in ECs. If the average δ^{15}N from this study is representative for all Si_3N_4 from ECs, other N-carriers with heavier N-isotopic compositions must be contributing significantly to the whole-rock compositions.

We determined Si_3N_4 abundances for several individual metal-sulfide nodules from PCA 91020 and Indarch, and found values ranging from 2,200 to more than 10,000 ppm, corresponding to N abundances from 880 ppm to >4,300 ppm. These concentrations are much higher than the maximum amount of N that can be introduced into liquid Fe metal under highly reducing conditions (~450 ppm at T ~1,300 K, $p(N_2)$ ~1 atm) [e.g., 16], although higher levels can be obtained under high-pressure conditions. However, such conditions do not constitute a likely formation scenario for N-bearing metal in the solar nebula, and both exsolution of Si_3N_4, from the metal or formation by impact processing do not appear to be viable scenarios.

TOF-SIMS analysis of the large nitride grain from Indarch confirmed the presence of O, which was initially indicated by EDS analysis. We also found small amounts of Cr, as well as Na and Ca in localized regions. Cr/Si ranges from $(5.6\pm0.6)\times10^{-3}$ to $(8.1\pm0.3)\times10^{-3}$ (0.4–0.6×CI), and for the upper part of the grain, we found Na/Si of $(3.1\pm0.1)\times10^{-3}$ (0.05×CI), together with Ca/Si of $(2.28\pm0.03)\times10^{-2}$ (0.4×CI). Two large Si_3N_4 grains (each several µm in diameter) from two different metal-sulfide assemblages in PCA 91020 were prepared by FIB and studied by TEM. Bright field imaging (BF-TEM), as well as selected area electron diffraction (SAED) analysis clearly showed that the grain is polycrystalline, with respective d values mainly corresponding to nierite (Fig. 2). They consist of a multitude of sub-grains with sizes of 100-500 nm. Besides unaltered Si_3N_4 grains with small (few nm in size) Ni-rich inclusions (schreibersite, perryite, taenite), areas that experienced varying degrees of alteration were found, as well as cracks that sometimes correspond to grain boundaries, indicating that the nitride grain experienced mechanical stress. The altered regions were identified as the major carrier of oxygen (as Fe oxides), while the still pristine and homogeneous areas did not contain significant amounts of O. A considerable fraction of the grains contain small amounts of S, while the surrounding Fe,Ni metal shows no S above detection limit.

Conclusions: Si_3N_4 grains from PCA 91020, Indarch, and Kota-Kota have light N-isotopic compositions with $\delta^{15}N_{avg} = (-62\pm1)$ ‰. The abundances of Si_3N_4 (and respective N concentrations) in individual metal-sulfide assemblages are too high to be explained by exsolution from the metal under nebular conditions. Two large silicon nitride grains were clearly identified as polycrystalline aggregates, consisting of a multitude of sub-µm-sized grains in various orientations. O is present in the grains as Fe oxides in the more altered regions. The high Si_3N_4 abundances in individual metal-sulfide nodules, the occurrence of polycrystalline grains, and the presence of S in unaltered Si_3N_4 grains (while absent in the surrounding metal) argue against grain formation by exsolution or parent body metamorphism, and seem to support a nebular origin.

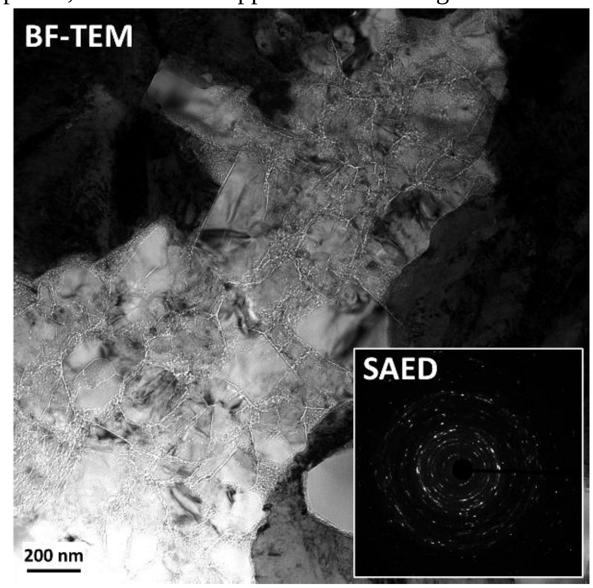

Figure 2. *BF-TEM image of grain PCA_H_2_1, with SAED pattern (inset) showing the polycrystalline structure. White lines in the BF image are cracks, likely caused by mechanical stress.*

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