IN SITU ISOTOPIC STUDY OF NITROGEN CARRIERS IN UNEQUILIBRATED ORDINARY CHONDRITES.

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Introduction: Nitrogen, the most abundant component in the terrestrial atmosphere, has been one of the key elements for the evolution of Earth's biosphere. The N-isotopic ratios of the terrestrial planets differ significantly from those of the Sun and the protosolar nebula [e.g.,1–3]. Thus, other nebular components must have contributed significantly to terrestrial N. Besides enstatite chondrites, ordinary chondrites (OCs) have been identified as suitable analogue material for the terrestrial building blocks [e.g., 4,5]. Whole-rock N-abundances between 1 and 160 ppm have been found [e.g., 6–8], and bulk δ^{15}N-values (relative to terrestrial air) range from –230 ‰ to +760 ‰ [8]. Organic material (OM) in OCs has bulk N-isotopic compositions between –50 ‰ and +60 % [9], i.e., less variability than on the whole-rock scale, indicating the presence of further N-carriers in the OCs with more extreme isotopic compositions. Previous studies reported graphitic carbon in a set of OCs of low petrologic type with N-isotopic anomalies corresponding to the heavy bulk-N-compositions [10,11]. Furthermore, small amounts (12 to 148 ppb) of Si_3N_4 were identified in three ordinary chondrites [12], but no comprehensive investigation of the inventory of N-carriers in OCs has been conducted to date. Here, we present first results of an ongoing isotopic and mineralogical study of organic and inorganic nitrogen-bearing phases in ordinary chondrites.

Methods: Polished sections of Semarkona (LL3.00) and Mezö-Madaras (L3.7) were characterized by 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 to identify potential N-carriers. The C- and N-isotopic compositions of suitable N-bearing phases were then measured by NanoSIMS at the MPIC by rastering a ~100 nm Cs^+ primary ion beam (~1 pA) over selected sample areas. Secondary ion images of $^{12,13}C^-$, $^{12}C^{14}N^-$, $^{12}C^{15}N^-$, and $^{28}Si^-$ were recorded in multi-collection mode.

Results and Discussion: Twenty-nine Si_3N_4 grains were identified by SEM-EDS investigation in a metal-sulfide-inclusion in Mezö-Madaras. The largest grain measures 830×360 nm, while 21 of the 29 nitrides are smaller than 300 nm in diameter. Twenty-eight grains were quantitatively investigated with SEM-EDS, and all grains contained Cr above detection limit, with Cr/Si atomic ratios ranging from 0.05 to 1.3. However, the Cr abundances especially for the smaller grains are clearly affected by Cr from the surrounding host metal, thus, further work is required for a proper characterization. Several of the larger nitrides contain resolvable subgrains in both BSE and EDS maps, suggesting they are rather Si_3N_4-CrN-intergrowths than Cr-bearing silicon nitrides. Six grains were subsequently measured by NanoSIMS. The δ^{15}N-values range from –236±147 ‰ to 10±25 ‰, with a weighted average of –27±14 ‰. The abundance of Si_3N_4 in the host grain is ~14 ppm, well below the values reported for individual metal-sulfide host grains in enstatite chondrites [13].

While organic matter in carbonaceous chondrites has been extensively studied with a variety of techniques, far less work has been conducted on OM in ordinary chondrites [e.g., 14,15]. Previous isotopic investigations of extracted insoluble OM showed large D-enhancements compared to the terrestrial value, while ^{15}N-enrichments appear to be much rarer than in the carbonaceous chondrite (CC) OM [14,15]. So far, ~1500 µm² of matrix material in Semarkona have been investigated, revealing six hotspots with δ^{15}N ranging from 350 ‰ to 1060 ‰ (4σ significance level), as well as one "cold spot" with a ^{15}N-depletion of –238±48 ‰. Further isotopic and structural analysis will be performed to allow a more thorough comparison between OC and CC organics. Extending this study to OM from other OCs, together with further investigation of inorganic N-carriers like Si_3N_4 and graphite will enable us to obtain a more comprehensive picture of the inventory of nitrogen carriers of these meteorites, which represent a good analogue material for a significant fraction of the terrestrial building blocks.

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