CARBONACEOUS N-ANOMALOUS GRAINS IN THE CO3.0 METEORITE ALHA77307. M. Bose, C. Floss, and F. J. Stadermann. Laboratory for Space Sciences and Physics Department, CB 1105, One Brookings Drive, Washington University, St. Louis MO, 63130, USA (mbose@physics.wustl.edu).

Introduction: Presolar material incorporated into the solar nebula, and found in various meteorites, consists of circumstellar stardust and interstellar material. The former is identified by large isotopic anomalies in the major and minor elements [e.g., 1], while the latter is most commonly identified by D and N isotopic anomalies [e.g., 2]. Carbon isotopic anomalies have also been observed in extraterrestrial materials but they are less common [e.g., 3]. The carbonaceous chondrite ALHA77307 has experienced a minimal amount of processing, which is evident from the high abundance of O-anomalous grains [4]. Here we report on N anomalies identified in the ALHA77307 matrix and their carrier phases.

Methods: A primary Cs^+ beam (< 1 pA) of ~100 nm diameter was used for ion imaging in the NanoSIMS. The beam was rastered over matrix areas in the ALHA77307 thin section. Secondary ions of $^{12}C^-$, $^{13}C^-$, $^{12}C^{14}N^-$, $^{12}C^{15}N^-$, and $^{28}Si^-$, as well as secondary electrons, were simultaneously acquired in multi-collection mode from 10×10 μm^2 areas for 5–10 consecutive scans. Isotopic ratios obtained from the bulk 10×10 μm^2 areas were used as a reference for internal normalization, assuming the terrestrial $^{14}N/^{15}N$ ratio of 272. The N-anomalous grains are present as localized hotspots in the matrix and the bulk $\delta^{15}N$ value of the insoluble organic matter (IOM) in ALHA77307 is 3 ‰ [5]; both make the methodology of internal normalization valid.

Subsequently, high-resolution secondary electron images and elemental spectra (30–2150 eV) were acquired from the ^{15}N-rich hotspots using a 10 keV electron beam in the Auger Nanoprobe. The primary current setting for the former measurements was 1 or 5 nA, while that for the latter measurements was 0.25 nA.

Results: Twenty-eight areas with N isotopic anomalies were identified in a total analysis area of 6700 μm^2. All the hotspots are localized spatially and exhibit ^{15}N excesses. Larger areas with enrichments in ^{15}N that are observed in other meteorites [e.g., 2] are absent in ALHA77307. The abundance of N isotopic anomalies, calculated on the basis of the size of the hotspots in the $\delta^{15}N$ images, is about 160±30 ppm.

The average $^{14}N/^{15}N$ ratio of all the hotspots is 169±8; the individual ^{15}N-rich hotspots have $\delta^{15}N$ values from 409–1266 ‰ (Fig. 1). Two ^{15}N-rich hotspots (D1 and E7-tp) exhibit ^{13}C-rich isotopic compositions with $\delta^{13}C$ values of 44±7 ‰ and 70±12 ‰. Although the N-anomalous hotspots exhibit a large scatter in the $^{12}C^-/^{28}Si^-$ elemental ratios, 67% of the N-anomalous hotspots have $^{12}C^-/^{28}Si^-$ ratios from 4–65. In contrast, isotopically normal areas surrounding the N-anomalous hotspots show $^{12}C^-/^{28}Si^-$ ratios of less than ~3. The CN^-/C^- ratios of the hotspots vary from 0.1 to 1.0 (Fig. 2). Although, the CN^-/C^- ratios of the hotspots generally increase with increasing $\delta^{15}N$ values, there is a large degree of scatter (Fig. 2). In addition, some hotspots do not exhibit this weak positive trend, e.g., four hotspots with large N anomalies cluster together, with low CN^-/C^- ratios of ~0.3.

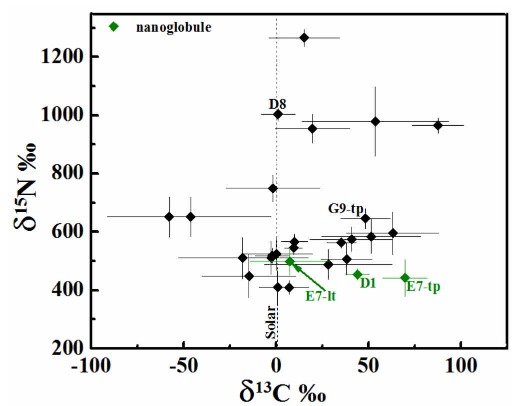

Figure 1: *Carbon and N isotopic compositions of the N-anomalous phases in ALHA77307. Nanoglobules are in green. Errors are 1σ.*

High-resolution secondary electron images of the ^{15}N-rich hotspots either show irregularly shaped matrix areas, which are larger than 350 nm in size, or show nanoglobule-like structures (Fig. 3). Auger spectra of the hotspots consist predominantly of C; some hotspots also show O, Si, Mg, and Fe Auger peaks. Quantification of the Auger spectra, considering the elements present in the hotspots, yield ~20 at.% O. In addition, the hotspots do not contain much N (< 3 at.%). Less than 2 at.% S is present in the hotspots.

Three nanoglobules have been identified in the matrix of ALHA77307 on the basis of their near-circular shapes and hollow structures. They are greater than 300 nm in size, and show mainly C in their spectra. Two of these (D1 and E7-tp) exhibit both N and C anomalies.

Discussion: The N-anomalous hotspots in ALHA77307 are heterogeneously distributed in the matrix. Although diffuse anomalies are absent in ALHA77307, the $\delta^{15}N$ values of the localized hotspots are similar in magnitude to those seen in other primitive meteorites [2].

The high $^{12}C^-/^{28}Si^-$ ratios and prominent C Auger peaks exhibited by the N-anomalous hotspots suggest that the carrier phase is carbonaceous in nature. In addition, Auger spectra of some hotspots contain O and Si, along with C, which suggests that the carbonaceous matter may be intimately associated with silicate material. The carbonaceous material identified in situ in ALHA77307 resembles IOM that has been extracted from meteorites in residue form [e.g., 2]. Presolar SiCs identified by ion imaging techniques exhibit $^{12}C^-/^{28}Si^-$ ratios of ~1, and therefore SiCs can be ruled out as the carrier phase of the N-anomalous phases based on the high $^{12}C^-/^{28}Si^-$ ratios of the hotspots. The presence of only small Si Auger peak in a few cases or its complete absence provides additional evidence against SiC as the carrier phase. Low-density presolar graphite with normal C and ^{15}N-rich isotopic compositions is a possible carrier of some N-anomalous hotspots [6]. In addition, the spherical morphology of graphite grains [6] is consistent with the near-circular shape of these hotspots. However, graphite grains with the aforementioned isotopic characteristics are rare. Although only mineralogical studies of the hotspots can conclusively constrain the carrier phase, carbonaceous phases formed in cold molecular clouds is a more likely carrier of the N anomalies. The N anomalies in the carbonaceous phases may be the result of low temperature ion-molecule reactions in cold molecular clouds [e.g., 7].

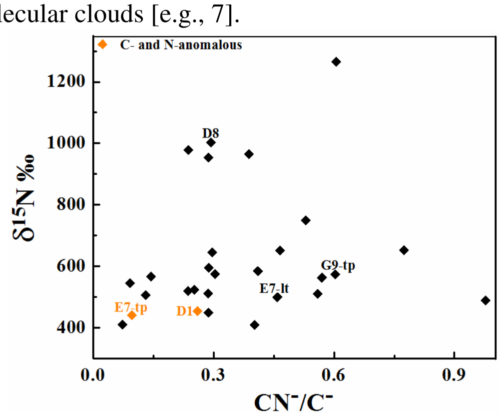

Figure 2: *CN^-/C^- ratios vs. N isotopic compositions of the carbonaceous phases.*

The nanoglobules, D1 and E7-tp, are similar in size to ones previously found [8, 9]. Most nanoglobules do not exhibit C anomalies [9]. However, the nanoglobules identified in this work show ^{13}C excesses, similar to one found in the CR3 chondrite MET 00426 [8]. The mechanism of nanoglobule formation is most likely an irradiation of interstellar grains that contain ice within them; subsequently, sublimation of the inner icy material may lead to the formation of hollow structures commonly observed in nanoglobules [9].

The CN^-/C^- ratios for the hotspots in ALHA77307 suggest N contents of less than 5 wt.%, based on the calibration curves of [10, 11]. The CN^-/C^- ratios vary a lot for the hotspots, which predominantly have $\delta^{15}N$ values roughly from 400–600 ‰. Six points plot significantly away from these hotspots (Fig. 2). None of the points that show elevated $\delta^{15}N$ values have different $^{12}C^-/^{28}Si^-$ elemental ratios or exhibit compositional differences from the other hotspots.

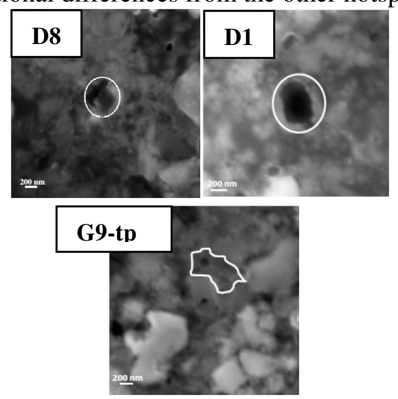

Figure 3: *High-resolution secondary electron images of a few ^{15}N-rich hotspots.*

Carbon isotopic anomalies, with associated N isotopic anomalies like those observed in this study have also been identified in other studies [e.g., 3, 8]. It has been speculated that the scarcity of C isotopic anomalies may be an indication of secondary processing, which may have destroyed the C-anomalous organic matter [e.g., 8]. ALHA77307 has experienced minimal processing based on Raman studies of its IOM [12]. The observations of abundant presolar grains [4] and N-anomalous phases [this work] lend additional support to this idea. However, ALHA77307's IOM with normal N-isotopic composition may be more altered than that of the CRs, which show bulk ^{15}N enrichments [5]. Furthermore, the absence of diffuse N anomalies spanning large areas of the matrix in ALHA77307, in contrast to that observed in other meteorites and IDPs [e.g., 2, 3], may suggest some alteration or destruction of its pristine organics.

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