Nitrogen isotopes in chondrules: Signatures of precursors and formation processes

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Nitrogen isotope abundance of 68 individual chondrules separated from six ordinary, two carbonaceous and two enstatite chondrites has been analysed. N composition of chondrules from ordinary and carbonaceous chondrites generally shows large variation and differs from that of their host. This large range of N composition suggests the presence of different N components in their precursors. Chondrules from the enstatite chondrites on the other hand show N isotopic composition similar to that of their host, suggesting precursors with similar N components for both chon-

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drules and their host meteorites. Nitrogen isotopic systematics therefore distinguishes chondrules in enstatite chondrites from those in ordinary and carbonaceous chondrites. Chondrules in ordinary and carbonaceous chondrites require precursors that are different from those of their parent meteorites and formation in nebular environment, whereas chondrules in enstatite chondrites are formed from the same precursors as those of their host chondrites and presumably in the same region.

Keywords: Chondrules, nebular process, nitrogen isotopes, parent-body process, precursors.

CHONDRULES are one of the earliest formed nearly spherical objects of about ~1 mm in diameter, with an abundance of up to 80% by volume in chondritic meteorites[1,2]. High abundance of chondrules implies that their formation was an important and common process during early stages of the solar system[3]. Petrological features suggest that chondrules are formed by flash heating and rapid cooling of pre-existing silicate precursors[1]. However, the mechanism of chondrule formation, and the nature of their precursors and environment(s) during their formation in different types of chondrites are poorly constrained. Many mechanisms have been proposed for the formation of chondrules, but none is completely satisfactory[4]. These mechanisms propose either nebular environment or planetary surface as the location of chondrule formation. For example, X-wind model[5] and nebular shock wave model[6] suggest chondrule formation in the nebula, whereas other models invoke different types of magmatic processes like volcanism and collisional events between planetesimals (with solid, partially molten or fully molten interiors) for chondrule formation[4].

Oxygen isotopic compositions of chondrules are different in different classes of chondrites and show large heterogeneity among and within chondrules[7,8]. The current interpretation of oxygen isotope data on chondrules advocates isotopic differences among chondrule precursors and survival of such precursors during the high-temperature chondrule forming event[9]. Isotopic compositions of nitrogen (δ^{15}N) also show distinct values for each class of chondrites[10]. Such isotopic evidences indicate different formation locations as well as heterogeneous precursors for chondrites. Ensembles of chondrules have been analysed for nitrogen from Soko-Banja[11] and Acfer 182 (ref. 12). Nitrogen in individual chondrules has only been investigated for Bjurböle[13] and Dhajala chondrites[14]. Here we report a systematic study of nitrogen isotope composition in individual chondrules separated from ten oridinary, carbonaceous and enstatite chondrites.

We have selected samples of petrologic class 3 or 4 of ordinary chondrites (OC) and enstatite chondrites (EC) and 2 or 3 of carbonaceous chondrites (CC), to minimize effects of parent-body processes (Table 1). For fragile chondrites, gentle disaggregation could dislodge chondrules, which were then sonicated to remove the adhering matrix. For tough or compact chondrites, a freeze–thaw method under vacuum was used to disaggregate the chondrules. Smaller splits from larger chondrules (weight >1 mg) were analysed for chemical and mineralogical compositions. Gas was extracted from individual chondrules by heating with Nd–YAG laser. An all-metal system with a small Pyrex glass branch line was designed for cleaning and separating the extracted gases with a low blank (~100 pg), as gas amounts from chondrules were extremely small[14]. Bulk chondrites were analysed by pyrolysis using a conventional glass extraction system. Gases extracted from both chondrules and the respective bulk chondrites were analysed for nitrogen and noble gases on a VG-1200 mass spectrometer[14,15]. The raw data have been corrected for blank contribution, mass interferences (by CO), and instrumental mass discrimination[15]. Blank correction in most cases was <5%, and seldom exceeded 20% (even for small sample size). A total of 68 chondrules coming from ten chondrites belonging to OC (6), EC (2) and CC (2) were analysed for nitrogen and noble gases, and the data are briefly summarized in Table 1 (complete dataset will be discussed in a separate manuscript under preparation). The masses of the chondrules (or splits) analysed were in the range of about 1 mg (0.2 mg and ~7 mg being the smallest and largest respectively). Splits for 26 of these chondrules have been analysed by EPMA for chemical and mineralogical characterization.

The nitrogen isotopic compostion was expressed using the δ-notation. $\delta^{15}N = [(R_{sample} - R_{standard})/R_{standard}] \times 1000$, where $R = {}^{15}N/{}^{14}N$. The standard for nitrogen is air (${}^{15}N/{}^{14}N = 0.003765$). The composition of trapped nitrogen ($\delta^{15}N_t$) was obtained by correcting the measured nitrogen composition ($\delta^{15}N_m$) for cosmogenic (cosmic ray-produced) contribution estimated from cosmogenic ^{21}Ne (${}^{21}Ne_c$). For average bulk compositions of the ordinary, enstatite and carbonaceous chondrites, it has been shown[16] that $({}^{15}N/{}^{21}Ne)_c = 4.5 \pm 0.5$. For individual chondrules, the chemical composition was used to derive the $({}^{15}N/{}^{21}Ne)_c$ ratio and for those chondrules for which chemical data is not available, the average chondrule composition for that class was used. Using the measured ${}^{21}Ne_c$ and the appropriate $({}^{15}N/{}^{21}Ne)_c$ ratio, the measured $\delta^{15}N_m$ was corrected for cosmogenic contribution[14]. The magnitude of correction depends on cosmic ray-exposure age and the N content of the sample, and ranged from <1 to 35% of the measured value.

From the $\delta^{15}N_t$ value of each of the chondrules and the corresponding bulk chondrite, we first calculated Δ^{15}N, defined as the difference between the values of each chondrule and the bulk ($\delta^{15}N_{chond} - \delta^{15}N_{bulk}$). If N composition of the chondrule was the same as that of its host, Δ^{15}N will be close to zero (or within ±10‰, for the class to which it belongs). Any value exceeding ±10‰ clearly indicates that N composition of the chondrule is

Table 1. Range of nitrogen composition and contents observed in chondrules

Sample (no. of chondrules analysed)	Range for chondrules		Values for two splits		Bulk	
	N (ppm)	$\delta^{15}N_t$ (‰)	N (ppm)	$\delta^{15}N_t$ (‰)	N (ppm)	$\delta^{15}N_t$ (‰)
Ordinary chondrites						
Dhajala (H3.8) (21)	0.8–35	–97 to 164	0.8, 5.9	–64, 39	2.2	–3.6
Udaipur (H3) (3)	4.5–8	23 to 63	–	–	6.1	–23
Tieschitz (H3.6) (5)	1.9–16	–5.6 to 97	–	–	10.2	–10
Saratov (L4) (3)	1.3–7.2	13 to 103	2, 7	13, 17	2.0	–8.8
Chainpur (LL3.4) (3)	7– 61	–9.6 to 8.1	25, 61	3.5, 4.7	*38.6 (f),* *31.3 (c)*	*2.1 (f),* *–2.6 (c)*
Bjurböle* (L/LL4) (8)	2.6–12	–8.7 to –134	–	–	*27*	*10*
Class range					1–50	–25 to 14
Enstatite chondrites						
Qingzhen (EH3) (4)	92–140	–22 to –28	112, 139	–28, –26	137	–28
Parsa (EH3) (3)	19–67	–21 to –31	67, 29	–21, –22	198	–31
Class range					50–300	–40 to –20
Carbonaceous chondrites						
Allende (CV3) (14)	2–11	–27 to 98	4, 4 7, 2	59, 82 18, 98	19,12	–36, –47
Murray (CM2) (4)	46 –77	59 to 116	–	–	643	40
Class range						
CV					20–170	–45 to 6
CM					600–1400	27 to 53

Values for respective bulk chondrites are also given for comparison. Out of the total 68 chondrules, two splits were analysed for seven chondrules. It was observed that splits of chondrules separated from ordinary and carbonaceous chondrites generally showed different values of nitrogen composition, whereas splits of enstatite chondrules showed similar N composition. Data given in italics for bulk are measured on matrix samples. *Data for matrix taken from Fredriksson *et al.*[13]. Errors in $\delta^{15}N$ (2σ) are ≤5%, and in N contents, ±10%. At the bottom of each chondrite class, the observed range of N and $\delta^{15}N$ is given (after Grady and Wright[10]).

different from the bulk. In Figure 1, the $\Delta^{15}N$ values are plotted for chondrules in each class of chondrites in separate panels. As can be seen in Figure 1 *a*, $\Delta^{15}N$ values of chondrules in OC show both positive and negative values. Twenty-one chondrules even within one meteorite, Dhajala, show $\delta^{15}N$ values with a large spread (–97 to +164‰), but their N contents are similar to the range observed for OC (Figure 1 *a*). The mean of $\Delta^{15}N$ for all the Dhajala chondrules falls in the range of bulk OC. The entire dataset for OC (46 chondrules from six ordinary chondrites) shows larger variations (~–134‰ to +164‰) of N compositions. Two splits from each of the three OC chondrules have been analysed. Surprisingly, the two splits show different N compositions as well as N contents (see Table 1). This indicates that N compositional heterogeneity within a chondrule has survived the chondrule formation process. This clearly suggests that the large spread of N compositions among the chondrules of OC is due to similar spread originally present among the OC chondrule precursors.

All chondrules from carbonaceous chondrites show heavier N compositions and lower amount of nitrogen, relative to the generally observed range in bulk carbonaceous chondrites (Figure 1 *b*). Sixteen chondrules analysed from Allende chondrite (a CV chondrite) had positive $\Delta^{15}N$ (ranging from 9 to 134‰) compared to bulk Allende and the range for CV chondrites. The amount of nitrogen was lower (maximum ~10 ppm) in chondrules compared to bulk CV chondrites. Four chondrules analysed from Murray chondrite (a CM chondrite) also showed positive $\Delta^{15}N$. Depletion of N in Murray chondrules was much higher than in Allende chondrules. The volatile rich matrix and the high matrix/chondrule ratio can account for these observations. Data for the splits of two Allende chondrules display heterogeneity, as in the case of OC chondrules.

In contrast, chondrules in Enstatite chondrites show $\Delta^{15}N$ similar to their host chondrites (Figure 1 *c*). $\Delta^{15}N$ in all the nine chondrules analysed from Parsa and Qingzhen chondrites ranged from 0 to 10‰, well within the range observed for bulk chondrites (Table 1). Also the splits of both Parsa and Qingzhen chondrules clearly show a homogeneous N composition in contrast to OC and CC. This implies that the N composition among the EC chondrule precursors is more homogeneous to begin with, and also similar to that of the enstatite chondrites.

In OC and CC, N composition of chondrules differs from their host and chondrules generally show ^{15}N enrichment. Variation in $\delta^{15}N$ is a consequence of partial nitrogen loss (plausibly during chondrule formation) from chondrule precursors (all of them initially having identical N and $\delta^{15}N$) and the associated isotopic fractionation (enrichment of ^{15}N in the residual reservoir); and then a trend of increased $\delta^{15}N$ with lower N content is expected. However, such a trend is not observed in case of chondrules from ordinary chondrites. Chondrules from Allende seem to indicate such a trend between their N composition and amount (Figure 1 *b*). To investigate this, we have calculated possible ^{15}N enrichment in chondrules due to mass-dependent loss of trapped molecular nitrogen from the chondrule precursors (for chondrule precursors, values of N content and $\delta^{15}N$ are assumed similar to the matrix). However, as shown in Figure 2, for Allende chondrules, enrichment of ^{15}N in residue (crystalizing chondrules) falls short of the observed values, which are up to ≥100‰. This suggests that mass-dependent nitrogen loss from chondrule precursors cannot explain the observed range of $\delta^{15}N$ values (compared to host) in chondrules.

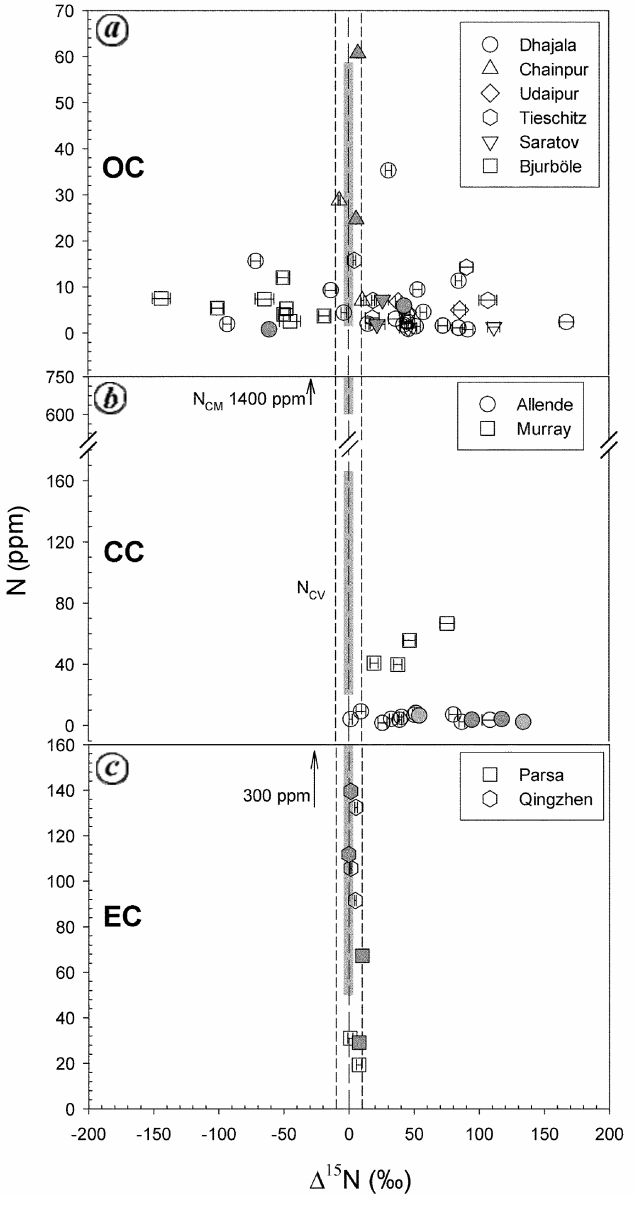

Figure 1. Plot of $\Delta^{15}N = (\delta^{15}N_{chond} - \delta^{15}N_{bulk})$ vs N for chondrules. ***a–c***, Data for ordinary, carbonaceous and enstatite chondrites respectively. The ±10‰ uncertainty lines around the zero value of $\Delta^{15}N$ cover the variation observed among bulk values for the class of chondrites represented in each panel. The thick band on the vertical line through $\Delta^{15}N = 0$ covers the range of N values observed for that class of meteorites (after Grady and Wright[10]). In (***b***) the N range for CM chondrites is shown separately, as it spans 600–1400 ppm. Values observed for splits of a single chondrule are shown in grey shade.

It has been suggested that in nebular shock wave model for chondrule formation, heating duration is proportional to the size of chondrule precursors[6]. This implies that larger chondrules may suffer greater loss of volatiles compared to smaller chondrules. This could establish a relation between size and abundance of volatiles in chondrules. However, neither $\delta^{15}N_t$ nor N content of individual chondrules from Dhajala, Bjurböle and Allende (for which larger number of chondrules have been studied) shows any apparent relation with chondrule size. The radii of the analysed chondrules (0.2–1 mm) have been estimated from its mass, assuming it a sphere with a density of 3.3 g cubic cm.

Also, splits of a single chondrule from OC and CC generally show different N compositions (Figure 1 *a* and *b*), favouring the presence of heterogeneous N components in different phases of chondrules. Hence, preservation of N isotopic heterogeneity of the chondrule precursors can best explain the trend observed for OC and CC chondrules. Similarity in N composition of chondrules from EC and their host suggests that precursors of chondrules were similar to their parent chondrites, implying the same environment of formation for chondrules and their parent E-chondrites. Homogeneity of $\delta^{15}N$ for the splits of Parsa and Qingzhen chondrules (Figure 1 *c*) further strengthens this contention. Such homogeneous nitrogen composition

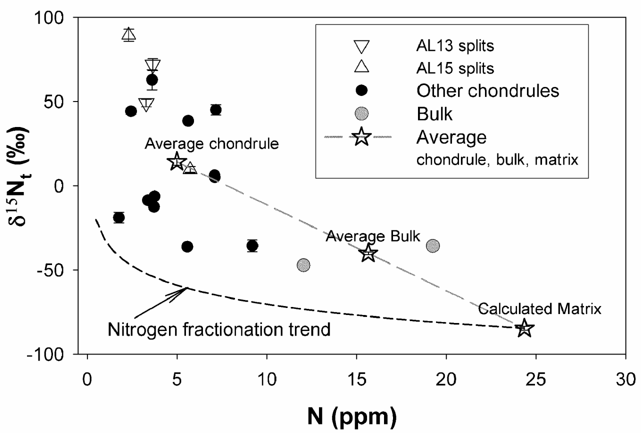

Figure 2. Plot of nitrogen composition and abundance of Allende chondrules. Nitrogen fractionation trend represents evolution of N composition based on Rayleigh loss of molecular nitrogen during chondrule formation. Based on average values of chondrules and bulk, N composition and content of matrix has been calculated by mass balance, for chondrules to matrix ratio of 55 : 45. These values are taken for chondrule precursors. The trend cannot explain the observed $\delta^{15}N$ values of chondrules and suggests the presence of ^{15}N-rich component ($\delta^{15}N$ > 100‰) to explain the data.

suggests formation of chondrules together or during the accretion of enstatite (chondrite/achondrite) parent bodies.

It is well established that enstatite chondrites have formed under more reduced environment compared to other chondrites. Nitrogen and oxygen compositions of EC are also distinct compared to OC and CC[10,17]. Compositional fractionations among EC and between the EC and the CI chondrites are greater than other chondrites. These two observations are explained by the formation of EC in the innermost part of the solar nebula[18]. A thermodynamic model proposed for the formation of EC to explain major chemical properties also argues their formation near or within the orbit of Mercury[19]. More recently, based on the observed radial gradient in ε^{53}Cr, it was inferred that the EC formed in zones closer to the sun (i.e. >1.0 to 1.4 AU)[20].

In addition, younger I-Xe ages of chondrules from Qingzhen (EH3) and Kota Kota (EH3) chondrites compared to Shallow Water (aubrite) suggest the existence of enstatite parent bodies during chondrule formation[21], indicating the possibility of formation of enstatite chondrules on parent bodies similar to EC. Petrological features of EC chondrules are consistent with their formation in a thick dynamic regolith on their parent body[22].

EC and the aubrites (enstatite achondrite) have similar nitrogen and oxygen isotopic composition[10,17] and therefore it is believed that they might have formed from a reservoir of similar composition, in the same region of the solar system[23]. Some plausible formation scenarios for the chondrules of EC could be as follows: The early-accreted EC had enough short-lived ^{26}Al and ^{60}Fe to melt and differentiate to produce parent bodies of aubrites[21]. Volcanic eruptions on these partially molten (still cooling) aubrite parent bodies (probably aided by impacts) could have resulted in the formation of silicate spherules (chondrules) that have been thrown into the neighbourhood. These chondrules must have become part of the enstatite parent bodies that subsequently accreted in the same region (based on similar oxygen and nitrogen isotopic compositions of EC and aubrites).

Nitrogen isotopic systematics of individual chondrules from OC, CC and EC suggests that chondrules from EC are formed by a different mechanism compared to those of OC and CC. This indicates that more than one process is needed to explain the formation of chondrules from all classes of chondrites. Normal isotopic fractionation and effects during chondrule formation cannot explain the N compositional range observed for chondrules of OC and CC. Such large variation indicates the presence of heterogeneous nitrogen components in the precursors and their survival during the chondrule-formation process.

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