N_2 self-shielding in the solar nebula as the mechanism of ^{15}N enrichment in meteoritic amino acids.

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Introduction: The presence of abundant amino acids in carbonaceous chondrite meteorites likely derives from both photochemical processes in the solar nebula and aqueous chemistry on meteorite parent bodies. In addition to the L-enantiomeric excesses that have been measured in some meteoritic amino acids (e.g., [1]), ^{15}N excesses have also been measured [2], [3]. Here, we propose that photochemical self-shielding of N_2 is responsible for the measured ^{15}N enrichments in meteoritic amino acids.

Meteoritic amino acids are typically enriched by ~ 50 - 200 ‰ in $\delta^{15}N$, measured relative to Earth atmosphere N_2 [2] (Fig. 1). However, this does not capture the full magnitude of the enrichment. Measurements of N isotopes in solar wind samples collected by the NASA Genesis mission reveal that inner solar system objects, including Earth's atmosphere, are enriched by ~ 400 ‰ compared to the bulk Sun [4] (Fig. 2). Therefore, the enrichment in meteoritic amino acids, relative to the starting material from which the solar system formed (the bulk Sun) is ~ 450 – 600 ‰, measured relative to Earth atmospheric N_2. Photochemical self-shielding of gas phase N_2 is capable of producing such massive ^{15}N enrichments.

N_2 self-shielding in the solar nebula: Photochemical self-shielding occurs for molecules with line-type absorption spectra. Such spectra are most common in diatomic molecules, such as CO or N_2. In such molecules the rotational transitions between electronic states generally have a line width << the line shift between isotopologues. Therefore, line saturation occurs first for the most abundant isotopologue, but not for the less abundant isotopologues. For gas phase N_2, $^{28}N_2$ becomes optically thick (saturated) in the solar nebula, but $^{29}N_2$ does not, so that ^{15}N atoms are liberated during photodissociation in far greater number than ^{14}N atoms. Incorporation of ^{15}N in ice phase HCN and NH_3 generates ^{15}N-enriched HCN and NH_3 on dust grains, which we designate as HCN_{gr} and NH_{3gr}.

Previous modeling of N isotopes in protoplanetary disks has demonstrated the dominance of N_2 self-shielding with respect to N isotope distribution. The reduction in photolysis rate of $^{28}N_2$ due to self-shielding is illustrated in the static disk model in the upper left panel of Figure 3 [5]. The model assumes an initial N_2 isotopic composition that is solar ($^{14}N/^{15}N$ ~ 400, Fig. 2), but because N_2 has 2 locations for N atom substitution, the initial isotopic ratio is $^{28}N_2/^{29}N_2$ ~ 200). N atoms and HCN, which is produced from N atom chemistry, both show lower $^{14}N/^{15}N$ ratios as a result of the high enrichment in ^{15}N due to preferential photolysis of $^{29}N_2$ (i.e. self-shielding by $^{28}N_2$) (Fig. 3). By contrast, NH_3 in the disk model shows an enrichment of ^{14}N (lower right panel of Fig. 3). This occurs because in this disk model [5] NH_3 is formed by a sequence of ion-molecule reactions starting with N_2, therefore the resulting NH_3 is depleted in NH_3.

We have completed initial modeling of N isotopes in a vertically-mixed solar nebula model that includes N_2 self-shielding and HCN and NH_3 formation in a network of over 700 reactions involving ~ 100 species [6]. We have included NH_3 formation on the surface of cold dust grains. In contrast to [5] we find NH_3 produced on grain surfaces (NH_{3gr}) to be highly enriched in ^{15}N, with delta-values relative to Earth atmosphere ranging up to +800 ‰ depending on various assumptions described in detail in [6]. The essential point is that the modeling demonstrates that N_2 self-shielding can easily achieve the ^{15}N enrichments observed in the inner solar system.

Amino acid formation: Amino acids in meteorites are formed primarily by aqueous phase reactions in their meteorite parent bodies. Numerous reaction mechanisms have been proposed, several of which are illustrated in Figure 4. Strecker synthesis, Michael addition, and reductive amination all involve reaction of a carbonyl or nitrile with NH_3. NH_3 that is derived by grain formation and N_2 self-shielding in the solar nebula will contribute its substantial ^{15}N enrichment to amino acids formed by these three formation mechanisms.

Conclusions: We argue here that the ^{15}N enrichment measured in meteoritic amino acids can be explained as a result of NH_3 production from N atoms liberated during N_2 self-shielding in the solar nebula. N_2 self shielding provides a natural mechanism for producing ^{15}N enrichments of ~ 400 to 600 ‰. N isotope fractionation due to additional parent body reactions will also occur but will be minor in comparison.

References

[1] Cronin J. R. and Pizzarello S. (1997) *Science*, 275, 951. [2] Elsila J. et al. (2012) *MAPS*, 47, 1517. [3] Glavin D. et al. (2020) *Chem. Rev.*, 120, 4660. [4] Furi E. and Marty B. (2015) *Nat. Geo.*, 8, 515. [5] Visser R et al. (2018) *Astron. Astrophys*. 615, A75. [6] Garani J. and Lyons J. R. (2021) *LPSC LII (this meeting).*

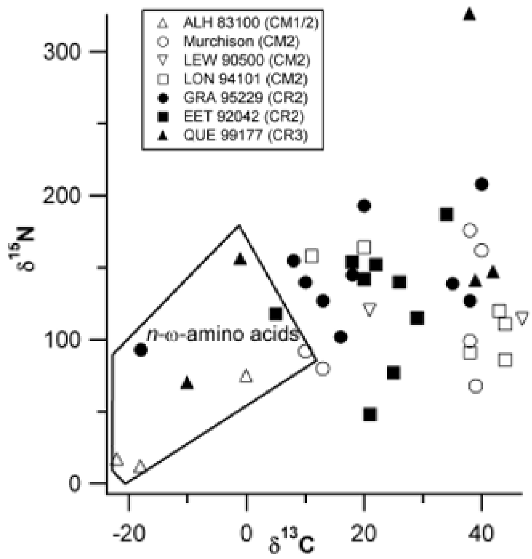

Fig. 1 *Isotopic data for amino acids in seven carbonaceous chondrites. Outlines areas highlight subsets of structurally similar compounds, which are not important for the present discussion. (Figure from Elsila et al. 2012 [2]).*

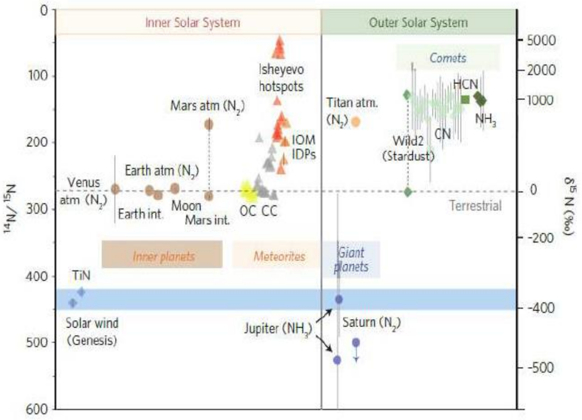

Fig. 2 *N isotopes in the solar system (Furi and Marty 2015 [4]). Isotopic reference is Earth atmosphere. The key point is that inner solar system objects are enriched in* ^{15}*N by about 400‰ compared to the Sun (light blue bar).*

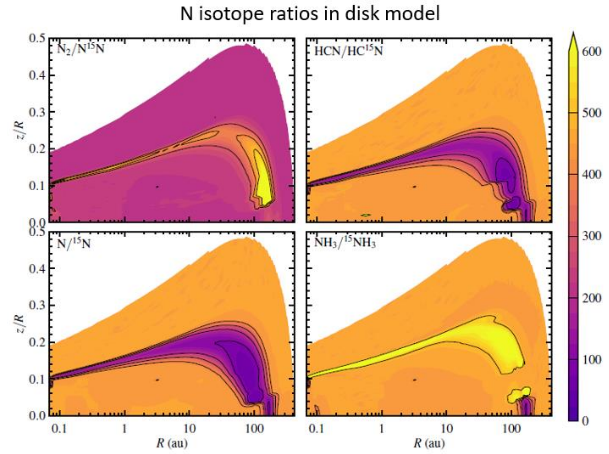

Fig. 3 *N isotope calculations for a static (no vertical mixing) disk model. The model shows a high* $^{14}N/^{15}N$ *ratio in* N_2 *due to self-shielding by* $^{28}N_2$*, and low* $^{14}N/^{15}N$ *ratios in atomic N and HCN also due to self-shielding. The* $^{14}N/^{15}N$ *ratio for* NH_3 *is predicted to be very high, which is inconsistent with the N isotope data from meteoritic amino acids. (Figure from Visser et al. 2018 [5]).*

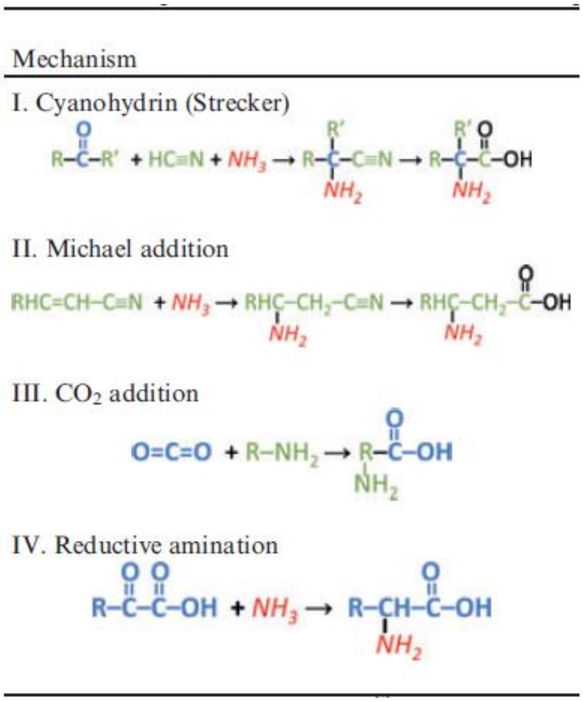

Fig. 4 *Several possible amino acid synthesis pathways proposed by Elsila et al. (2012)[2]. In 3 out of 4 of these pathways, the amine group derived from* NH_3*. Therefore, the isotopic composition of* NH_3 *is key to understanding* $\delta^{15}N$ *of meteoritic amino acids.*