

**A MOLECULAR CLOUD ORIGIN FOR N ISOTOPE ENRICHMENTS IN THE SOLAR SYSTEM, AND IMPLICATIONS FOR ENANTIOMERIC EXCESS IN AMINO ACIDS.** J. R. Lyons<sup>1</sup>, <sup>1</sup>Planetary Science Institute, Tucson, AZ, USA, jlyons@psi.edu.

**Introduction:** The enormous range of the N isotope ratio in solar system materials is well documented. Hot spots in meteorites show <sup>15</sup>N enrichment of up to several 1000 permil [1]. Jupiter and solar wind are depleted in <sup>15</sup>N by ~ 400 permil [2], [3]. Amino acids, inner solar system planets, comets, bulk meteorites and other planetary objects have <sup>15</sup>N/<sup>14</sup>N that reside between these two extremes [4]. N<sub>2</sub> self-shielding in the solar nebula produces NH<sub>3</sub> ice with the necessary <sup>15</sup>N enrichment, but only if there is no dilution by parent cloud ices [5]. Here, I discuss dilution in more detail, and qualitatively include low-temperature ion-molecule reactions. Because self-shielding is driven by UV photons, I also consider possible constraints on the generation of enantiomeric excess in chiral molecules by the UV radiation field.

**NH<sub>3</sub> ice fraction in parent cloud:** Figure 1 shows measured and assumed values for NH<sub>3</sub>/H<sub>2</sub> in various astrochemical environments. The NH<sub>3</sub> ice fraction is typically ~ 10<sup>-5</sup> or more, although there are few absolute measured value for ices.

**Inheritance from molecular cloud:** Accretion of ices onto the outer disk will result in ice sublimation [6], but should not isotopically scramble the inherited material. An initial cloud ice fraction > 10<sup>-6</sup> is then sufficient to dilute the effects of N<sub>2</sub> in the solar nebula (Fig. 2). If instead, N<sub>2</sub> self-shielding occurred in the parent cloud, <sup>15</sup>N enriched ices would be inherited by the outer solar nebula. Based on <sup>17</sup>O and <sup>18</sup>O isotope enrichment computed for CO self-shielding in a collapsing cloud core [7], I expect that N<sub>2</sub> self-shielding in the cloud can account for the <sup>15</sup>N enrichment of the inner solar system (Figure 3).

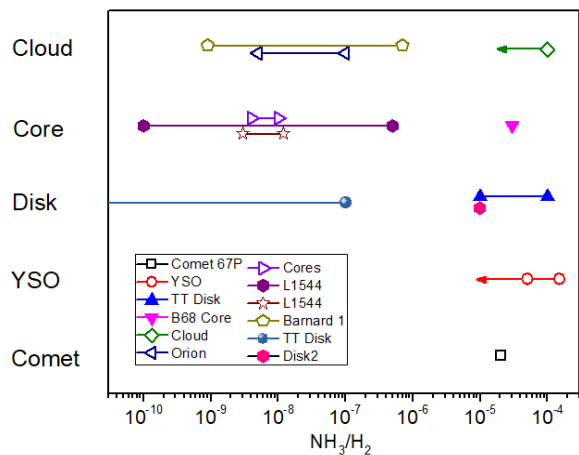
**Low-temperature ion-molecule reactions:** Model calculations of N<sub>2</sub> self-shielding do not produce <sup>15</sup>N enrichments large enough to account for hotspots. Experiments do reach such high δ<sup>15</sup>N values, but for conditions that are not astrochemically plausible [8]. These ultra-high enrichments can also result from ion-molecule reactions at temperatures low enough for CO condensation [9]. Dust temperatures in a collapsing core model are dependent on the external radiation field (Fig. 4). Prior to collapse (t = 0), dust temperatures in the inner core collapse zone are consistent with CO condensation and high and ultra-high fractionation due to both self-shielding and ion-molecule chemistry.

**Formation of enantiomeric excess by UV:** Meteoritic amino acids are strongly enriched in <sup>15</sup>N [10],

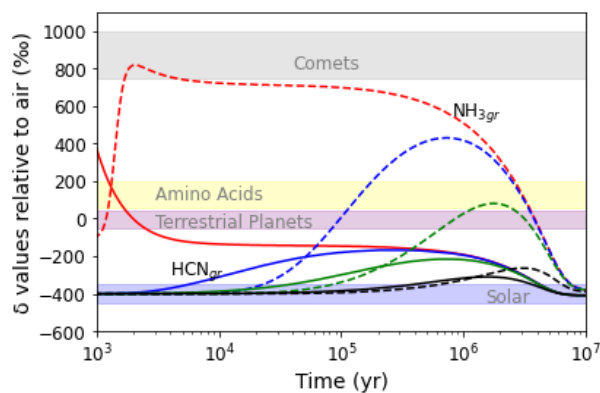
and some of them have an enantiomeric excess (e.e.) [11]. The most likely mechanism for creation of enantiomeric excess in chiral molecules in space is selective destruction by circularly polarized (CP) UV light. CP light is produced by scattering of starlight from magnetic field-aligned, helical dust grains [12]. The relative timescales for Larmor precession about the local B field,  $t_B$ , and for precession about the radiation field vector,  $t_k$ , determine dust grain alignment. For Orion molecular cloud (OMC), outer disk, and ISM conditions, a radiation field of  $G_0 < 10^4 - 10^5$  corresponds to  $t_B \ll t_k$ , and so is consistent with generation of CP light by scattering from field-aligned dust grains. Thus, UV light in a collapsing cloud core environment can be responsible for both <sup>15</sup>N enrichment of amino acids due to <sup>15</sup>N enrichment of NH<sub>3</sub> by N<sub>2</sub> self-shielding, and for generation of an e.e. in chiral amino acids by a circularly polarized UV radiation field.

**Conclusions:** Although self-shielding of N<sub>2</sub> is an effective <sup>15</sup>N enrichment mechanism for N-containing ices in the solar nebula, dilution due to inheritance from the parent cloud makes nebular self-shielding an implausible mechanism for explaining inner solar system <sup>15</sup>N enrichment. Instead, N<sub>2</sub> self-shielding in the parent cloud, followed by nebular inheritance, is a more likely explanation. The ultra-high <sup>15</sup>N enrichments in meteoritic hot spots probably arise from ion-molecule reactions at temperatures < 10 K. Creation of enantiomeric excesses in chiral molecules such as amino acids by scattering of stellar UV light requires radiation field intensity  $G_0 < 10^5$ , which is consistent with N<sub>2</sub> self-shielding. Simultaneous <sup>15</sup>N enrichment and enantiomeric selection is possible for the parent cloud, possibly via UV illumination of <sup>15</sup>N-enriched ices [13].

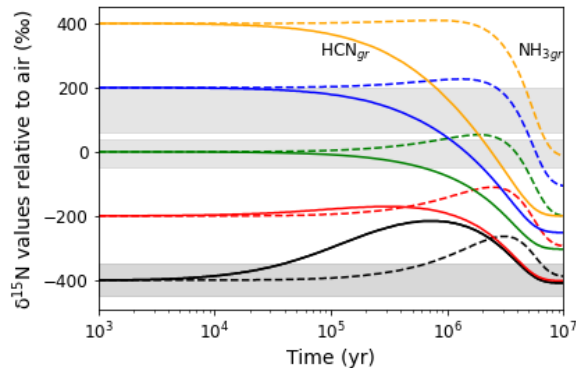
**References:** [1] Busemann, H. et al. (2006) *Science*, 312, 727. [2] Owen T. et al. (2001) *Astrophys. J. Lett.*, 553, L77. [3] Marty, B. et al. (2011) *Science*, 332, 1533. [4] Furi, E and Marty, B. et al. (2015) *Nat Geo*, 8, 515. [5] Garani J. and Lyons J. R. (2021) LPSC LII, abstract #2571. [6] Lunine, J. I. et al. (1991) *Icarus* 333-344. [7] Lee, J.-E. et al. (2008) *Meteorit. Planet. Sci.*, 43, 1351. [8] Chakraborty, S. et al. (2014) *PNAS*, 111, 14704. [9] Rodgers S. D. and Charnley S. B. (2008) *Astrophys. J.*, 689, 1448. [10] Elsila J. et al. (2012) *MAPS*, 47, 1517. [11] Glavin D. et al. (2020) *Chem. Rev.*, 120, 4660. [12] A. Lazarian (2007) *Elsevier BV*, 225-256. [13] Bernstein, M.P. et al. (2002) *Nature*, 416, 401. [14] Lee et al. (2004) *ApJ*, 617, 360.



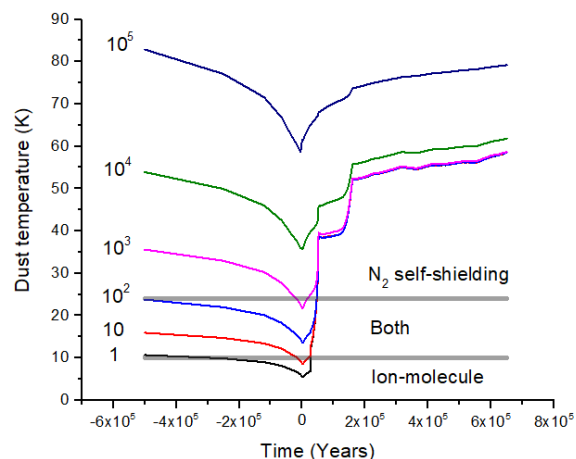
**Figure 1.** Published volume abundance ratio of  $\text{NH}_3$  gas and ice relative to  $\text{H}_2$ . Observations are shown with open symbols, and model values are shown with filled symbols.  $\text{NH}_3/\text{H}_2 < 10^{-6}$  correspond to gas phase values, while a ratio  $> 10^{-5}$  is for  $\text{NH}_3$  ice relative to  $\text{H}_2$  gas. Based on the plotted ratios, I conservatively assume a maximum initial  $\text{NH}_3$  ice abundance in the parent molecular cloud of  $10^{-5}$  relative to  $\text{H}_2$ . A complete list of citations for this figure will be given elsewhere.



**Figure 2.**  $\delta$ -values for  $\text{HCN}_{gr}$  (solid lines) and  $\text{NH}_3_{gr}$  (dotted lines) at the midplane for  $\alpha=0.01$  and  $G_0 \sim 500$  for different initial values of  $\text{HCN}_{gr}$  and  $\text{NH}_3_{gr}$ .  $G_0$  is the radiation field intensity relative to the local interstellar field, and  $\alpha$  is the strength of turbulent vertical mixing. The initial cloud values for mixing ratios of both species are  $10^{-5}$  (black),  $10^{-6}$  (green),  $10^{-7}$  (blue), and 0 (red), and the cloud ices have  $\delta^{15}\text{N} = -400\text{‰}$  (solar value). Inheritance from the molecular cloud causes dilution of  $^{15}\text{N}$  enrichment produced by self-shielding in the solar nebula for initial cloud  $\text{NH}_3/\text{H}_2 > 10^{-6}$ , making it impossible to reach terrestrial planet bulk  $\delta^{15}\text{N}$  values.



**Figure 3.**  $\delta^{15}\text{N}$  values of  $\text{HCN}_{gr}$  (solid lines) and  $\text{NH}_3_{gr}$  (dashed lines) in the midplane of the solar nebula at 30 AU for varying initial  $\delta^{15}\text{N}$  values for  $\text{HCN}_{gr}$  and  $\text{NH}_3_{gr}$  in the parent cloud. Initial cloud abundance is  $1 \times 10^{-6}$  for  $\text{HCN}_{gr}$  and  $1 \times 10^{-5}$  for  $\text{NH}_3_{gr}$ . The initial  $\delta^{15}\text{N}$  values ( $10^3$  years) represent different contributions of  $\text{N}_2$  self-shielding in the cloud, with  $-400\text{‰}$  being the solar value with no self-shielding. A 400 - 600  $\text{‰}$  initial enrichment relative to solar can account for terrestrial planet and meteoritic amino acid values. Shaded bars are defined as in Figure 2.



**Figure 4.** Evolution of dust temperature at the inner edge of a collapsing cloud core model as a function of radiation field  $G_0$ .  $G_0$  labels are to the left of each dust temperature curve. The dust temperature evolves during both the core densification phase (time  $< 0$ ) and the collapse phase (time  $> 0$ ), reaching a minimum at the start of collapse. The upper horizontal bar indicates the CO condensation temperature of 24 K. The lower horizontal bar indicates the temperature below which ion-molecule isotope exchange reactions produce massive  $^{15}\text{N}$  enrichment [9]. For  $G_0 > 10^3$ , CO remains in the gas phase at all time and  $\text{N}_2$  self-shielding is the primary source of massive  $^{15}\text{N}$  enrichment.  $G_0 \sim 10 - 10^3$  allow for  $^{15}\text{N}$  enrichment from both  $\text{N}_2$  self-shielding and ion-molecule reactions in the pre-collapse phase. Dust temperature curves are from [7] and [14].