MOLECULAR TRACERS OF NITROGEN ENRICHMENT IN PRESTELLAR CORES: AMINES VS. NITRILES.

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Introduction: A central issue for Solar System origins is the relationship between the chemical composition of star-forming interstellar clouds and that of primitive Solar System materials. Significant 15-nitrogen enrichments, relative to a nominal interstellar $^{14}N/^{15}N$ ratio of 400, have been measured in molecules found in comets and meteorites (Table 1, [1,2]). The pronounced ^{15}N enrichment in comets originating from distinct nebular formation zones (i.e. the Oort cloud and Jupiter family, JFCs) suggests that the origin of this fractionation is to be found in the natal molecular cloud core [1]. Early chemical models of interstellar fractionation in cold CO-depleted cores [3] predicted a general ^{15}N enhancement for nitriles, as well as amines. Table 1 shows that while recent interstellar observations support ^{15}N enrichments for nitrile species [4,5], this enrichment pattern has not been observed for NH_3[6]. Our more recent theoretical work [7] has shown that, once the spin-state dependence of ion-molecule reactions is considered (via the ortho-para ratio of H_2), significant time-dependent ^{15}N fractionation can be produced for NH_3. In fact, while HCN is enriched in ^{15}N within ~10^5 years, NH_3 is first depleted, before becoming enriched after 10^6 years (see Fig. 1).

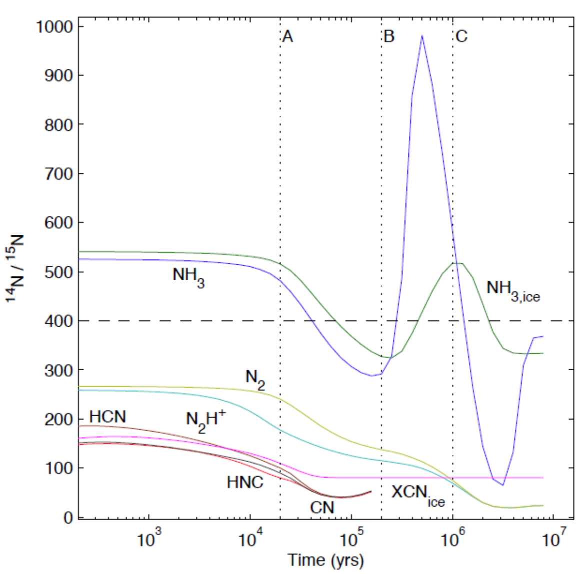

Figure 1. Nitrogen fractionation in gas-phase molecules and bulk ammonia and nitrile ices. From Wirstrom et al. (2012).

Thus, a potential bonus of these studies is that fractionation levels in different N-bearing molecules could provide an accurate molecular clock of the evolution of dense cores and protostars. However, a major problem is that N_2 is expected to be the dominant molecular form of nitrogen in dense clouds. Molecular nitrogen $^{14}N/^{15}N$ ratios, measured via N_2H^+, $^{15}NNH^+$ and $N^{15}NH^+$, have only been determined in two objects (Table 1, adapted from Milam & Charnley 2012). Whilst this provides some limited observational evidence for a correlation between the $^{14}N/^{15}N$

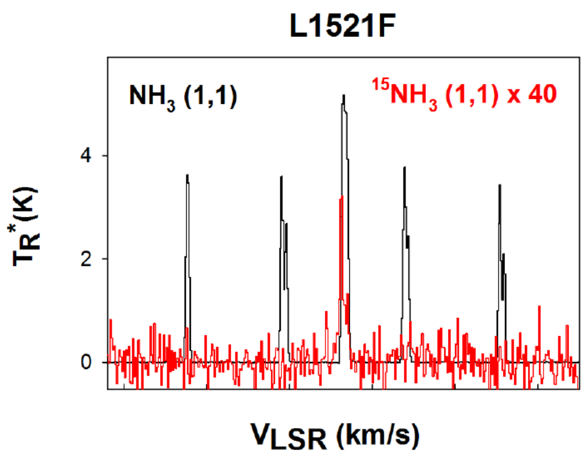

Figure 2. Spectra of the (J,K) = (1,1) transition of NH_3 and $^{15}NH_3$ taken with the NRAO GBT telescope (Adande et al. 2015, in preparation.)

ratio in ammonia and N_2, theoretical models actually predict that N_2 (and thus N_2H^+) should be as enriched as the nitriles (Figure 1), rather than be depleted!

More measurements of amines and their isotopologues in more sources are necessary to confirm and explore these trends further. We have recently initiated an observing campaign (see Table 1) to measure $^{14}N/^{15}N$ in HCN and HNC (at the ARO 12m and OSO 20m) and NH_3 (at the NRAO GBT, see Figure 2). These observations provide a preliminary, yet comprehensive, picture of $^{14}N/^{15}N$ in these sources for comparison with existing observations, cometary data and theory.

Observations: Observations have been conducted at centimeter, millimeter and submillimeter wavelengths employing various facilities in order to both spatially and spectrally, resolve emission from these cores. The data were collected at the Arizona Radio

Table 1: Interstellar & Cometary Nitrogen Isotope Ratios

Source	Type	NH_3	N_2H^+	HCN	HNC	CN	Reference
L1544	dark core	>700	1000±200	140-360	**>27**	500±75	1,2,3,4,5
L1498	dark core	**619±100**	...	**>75**	**>90**	500±75	11,4,4,5
L1521E	dark core	...	...	151±16	...	...	6
L1521F	dark core§	**539±118**	...	**>51**	**24-31**	...	11,4,4
L183	dark core	$530\pm^{570}_{180}$	...	140-250	...	...	1,3
NGC 1333-DCO$^+$	dark core	$360\pm^{260}_{110}$	...	...	...	...	1
L1262-core	dark core	**356±107**	...	...	...	...	11,3
NGC 1333-4A	Class 0 protostar	344±173	...	...	...	...	7
Barnard 1	Class 0 protostar	$300\pm^{55}_{40}$	$400\pm^{100}_{65}$	$330\pm^{60}_{50}$	$225\pm^{75}_{45}$	$290\pm^{160}_{80}$	8
L1689N	Class 0 protostar	$810\pm^{600}_{250}$	...	...	...	...	4
Cha-MMS1	Class 0 protostar	...	...	...	135	...	9
IRAS 16293A	Class 0 protostar	...	...	163±20	242±32	...	10
R Cr A IRS7B	Class 0 protostar	...	...	287±36	259±34	...	10
OMC-3 MMS6	Class 0 protostar	...	...	366±86	460±65	...	10
L1262-YSO	Class I protostar	**453±247**	...	...	...	...	11,3
Comets	JFC & Oort Cloud	127‡	...	139±26	...	135-170†	12,13,14

Boldface entries are unpublished values from our ongoing observational programme. Note that we have recently observed the relevant isotopologues of HCN and HNC at the L1262 positions at Onsala; these data are currently being reduced.

§ L1521F does contain a very low luminosity object (VeLLO, Bourke et al. 2006).

† Based on optical observations of HCN daughter molecule CN. This range can be taken as a surrogate for the HCN ratio, however in comets there may be additional sources of CN radicals unrelated to HCN, such as decomposition of macro-molecular organic matter (see Mumma & Charnley 2011). Only 2 measurements have been made for in HCN itself, in OC comets Hale-Bopp and the JFC comet 17P/Holmes.

‡ `Average' based on optical observations of NH_3 daughter molecule NH_2 in an ensemble of comets.

Observatory's 12m telescope on Kitt Peak, AZ, the Submillimeter telescope on Mt. Graham, AZ, and the National Radio Astronomy Observatory 100m telescope in Green Bank, WV. Spectra were obtained at high resolution (typically <0.2 km/s) in order to resolve dynamic properties of each source as well as to resolve hyperfine structure present in certain isotopologues (see Figure 1). Multiple transitions are being measured (when possible) to confirm abundances for those isotopologues that do not exhibit resolved hyperfine structure with radiative transfer models.

Results and Discussion: Significant variation is measured between nitriles and amines in the dark core L1544, while those in the Class 0 protostar, Barnard 1, seem fairly consistent with much smaller discrepancy. The trends observed to date in other dark cores seems consistent in a significant difference between $^{14}N/^{15}N$ in nitriles vs amines. These initial $^{14}N/^{15}N$ ratios show significant fractionation in the nitrile species compared to the other molecules within each object. Furthermore, the derived $^{12}C/^{13}C$ ratio from HCN towards L1544 is ~88, not the typically employed value of 67 obtained from the nearby interstellar medium. The extremely low values of $^{14}N/^{15}N$ in nitriles and the higher $^{12}C/^{13}C$ ratios measured are comparable to those obtained in comets and IDPs.

Further results and comparisons between the protostellar evolutionary state and solar system bodies as well as the variations in molecule specific isotope fractionation will be presented.

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