Nitrogen Isotopic Fractionation in Primitive Materials: Quantifying the Contribution of Interstellar Chemistry

Steven Charnley, Eva Wirström[1], Gilles Adande, Stefanie Milam & Martin Cordiner

NASA Goddard Space Flight Center, Astrochemistry Laboratory, Code 691, Greenbelt, MD 20771, USA

[1] Department of Space, Earth and Environmental Sciences, Chalmers University of Technology, Sweden

Abstract

Organic material found in meteorites and interplanetary dust particles is enriched in D and ^{15}N (Lauretta & McSween 2006). This is consistent with the idea that the functional groups carrying these isotopic anomalies, nitriles and amines, were formed by ion-molecule chemistry in the parent molecular cloud core. Theoretical models of interstellar fractionation at low temperatures predict large enrichments in both D and ^{15}N and can account for the largest isotopic enrichments measured in carbonaceous meteorites. We briefly summarise the current state of theoretical modeling of ^{15}N fractionation. We also summarise astronomical observations of $^{14}N/^{15}N$ ratios and demonstrate how these can be used to constrain theoretical models.

Theoretical Models

Theoretical models of nitrogen isotopic chemistry in molecular cloud cores, where gaseous molecules are being depleted by accretion on to dust grains, have been able to reproduce the range of $^{14}N/^{15}N$ enriched ratios found in primitive matter (~ 50-280, relative to a Solar value of 440; Figure 1) through exchange reactions between ^{15}N atoms and molecular ions such as $^{14}N_2H^+$ and $HC^{14}NH^+$ (see Figure 2, Charnley & Rodgers 2002; Rodgers & Charnley 2008). These models predict that N_2, NH_3, HCN, CN and HNC molecules should possess the greatest ^{15}N enrichments, and that there are two ^{15}N -fractionating pathways: a slow one to N_2 and ammonia (~10^6 years) and more rapid one to HCN and other nitriles (~10^5 years).

Theoretical models of interstellar fractionation at low temperatures predict large enrichments in both D and ^{15}N. However, measurements have shown that, in some primitive samples, a large ^{15}N enrichment does not correlate with one in D, and that some D-enriched primitive material displays little, if any, ^{15}N enrichment (e.g. Aleon 2010). Wirström et al. (2012) showed that the fractionation of ^{15}N may, like D fractionation (Pagani et al. 2011), be influenced by the H_2 ortho-to-para spin ratio (OPR). Ammonia formation is initiated by the production of N^+ from H_2 by He^+ (Figure 2), and the small activation energy in the subsequent reaction with H_2 can be overcome by the internal energy of *o*-H_2, a distinction not made in earlier models (e.g. Rodgers & Charnley 2008). These calculations demonstrated that the precise abundance of *o*-H_2 can play a pivotal role in producing a diverse range of D-^{15}N fractionation in molecular clouds (Wirström et al. 2012), in agreement with the meteoritic record.

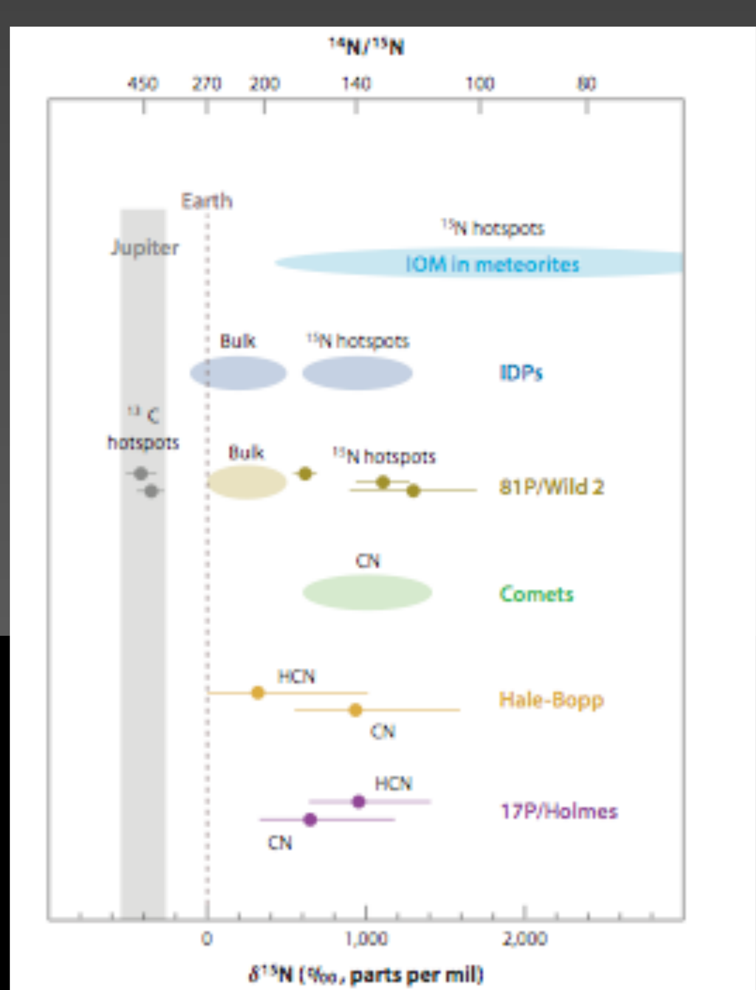

Figure 1. $^{14}N/^{15}N$ ratios in Solar System primitive matter. From Mumma & Charnley (2011).

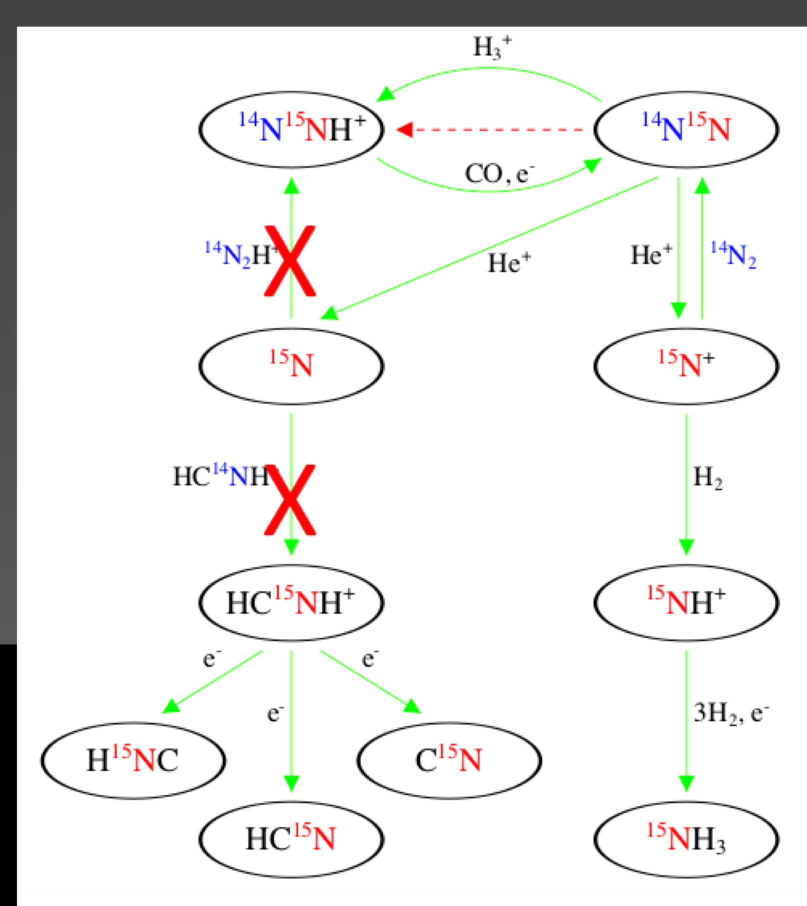

Figure 2. Chemical network showing the main reactions responsible for ^{15}N fractionation in interstellar nitriles and ammonia in the model of Wirström et al. (2012). Crosses denote pathways where quantum chemical calculations indicate the presence of small activation energy barriers (Roueff et al. 2015).

However, recent quantum chemical calculations by Roueff et al. (2015) indicate that key fractionation reactions in fact possess small activation energy barriers (denoted by crosses in Figure 2), making them inefficient at very low temperatures. Figures 3 (Wirström & Charnley 2018) show model calculations comparing the original model of Wirström et al. (2012) with a revised model using rate coefficients containing the energy barriers of Roueff et al.(2015). Clearly, the presence of these activation energies presents a serious challenge for ion-molecule fractionation chemistry.

This suggests that either a revaluation of the Roueff et al. calculations at a higher level of theory is required, or that alternative fractionation pathways be sought, perhaps involving neutral-neutral reactions (Wirström & Charnley 2018), isotope photochemistry, or gas-grain processes (Furuya & Aikawa 2018).

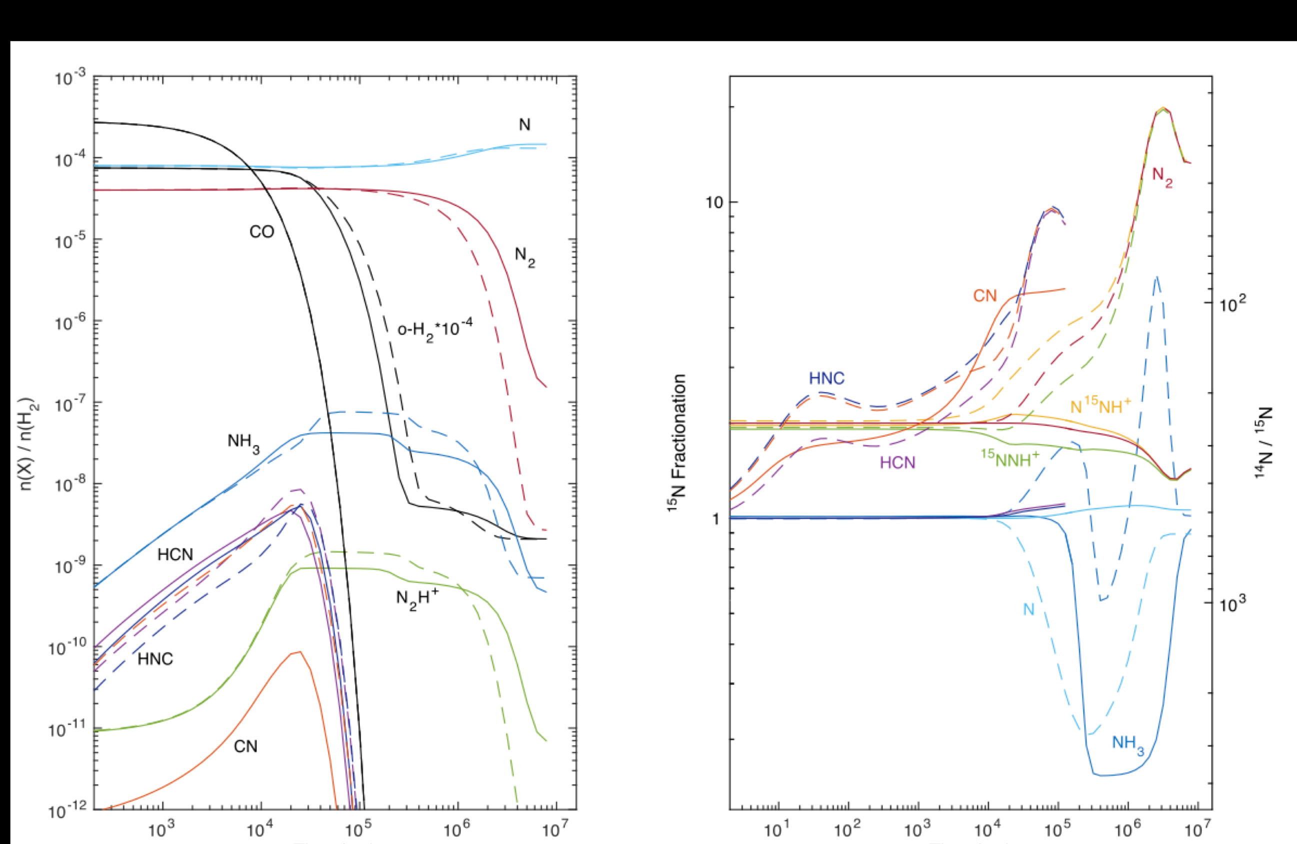

Figure 3. *Left panel*: Time evolution of the nitrogen chemistry in dense cores from Wirström et al. (2012) is shown as dashed curves. The revised model with rates from Roueff et al. (2015) and an updated nitrogen chemistry is shown as solid curves. *Right panel*: As Figure 3 but for the evolution of the ^{15}N fractionation in gas-phase molecules. On the left-hand axis the ^{15}N enrichment is given relative to a value of 1/440 while the scale on the right-hand axis gives the corresponding $^{14}N/^{15}N$ ratio. From Wirström & Charnley (2018).

Observations of Interstellar $^{14}N/^{15}N$ Ratios

Relevant astronomical observations of $^{14}N/^{15}N$ ratios in the ISM and comets are summarized in Table 1 (see Wirström et al. 2016). These indicate that interstellar HCN and HNC are found, as predicted, to be highly enriched in ^{15}N. On the other hand, N_2 and NH_3, show a large range of which the most depleted (largest) values are not predicted by current theory.

Observed $^{14}N/^{15}N$ Ratios in Molecular Clouds

TABLE 5
INTERSTELLAR NITROGEN ISOTOPE RATIOS

Source	Type	NH_3	$N_2H^{+\S}$	HCN	HNC	CN	Reference
L1544	dark core	>700	1000±200	**69-154**	**>27**	500±75	4,1,3,3,9
			1000±200	140-360			1,2
L1498	dark core	**619±100**	...	**>75**	**>90**	500±75	3,3,3,9
				>813			5
L1521E	dark core	...	...	151±16	...	...	5
L1521F	dark core	**539±118**	...	**>51**	**24-31**	...	3,3,3
L1262-core	dark core	**356±107**	**>450**	...	...	...	3,3
			>450				3
L183	dark core	$530\pm^{570}_{180}$	...	140-250	...	...	4,2
NGC 1333-DCO⁺	dark core	$360\pm^{260}_{110}$	...	...	...	...	4
NGC 1333-4A	Class 0 protostar	344±173	...	...	...	...	6
		>270					4
B1	Class 0 protostar	300	>600	165	75	240	10,10,10,10,9
		334±50	400				6,10
L1689N	Class 0 protostar	$810\pm^{600}_{250}$	...	...	...	...	4
Cha-MMS1	Class 0 protostar	...	...	...	135	...	7
IRAS 16293A	Class 0 protostar	...	...	163±20	242±32	...	13
R Cr A IRS7B	Class 0 protostar	...	...	287±36	259±34	...	13
OMC-3 MMS6	Class 0 protostar	...	...	366±86	460±65	...	13
L1262-YSO	Class I protostar	**453±247**	**>430**	...	...	...	3,3
			>430				3
Several	Massive starless cores	...	65-1100	...	...	330-400	15,15
			180-1034#				15
Orion-KL Hot Core	Massive protostar	$170\pm^{140}_{80}$	...	...	...	...	16
Several	Massive protostars	...	190-1000	...	...	190-450	15,15
			180-1300				15
Several	Ultracompact HII regions	...	320-900	...	...	230-430	15,15
			350-700				15
Comets	JFC & Oort Cloud	127‡	...	139±26	...	135-170†	11,12,8

References: (1) Bizzocchi et al. (2013); (2) Hily-Blant et al. (2013a); (3) Milam & Charnley (2012), Adande et al. (2016); (4) Gerin et al. (2009); (5) Ikeda et al. (2002); (6) Lis et al. (2010); (7) Tennekes et al. (2006); (8) Hutsemékers et al. (2008); (9) Hily-Blant et al. (2013b); (10) Daniel et al. (2013), lower limit is for the $^{15}NNH^+$ isotopologue ; (11) Rousselot et al. (2014); (12) Bockelée-Morvan et al. (2008); (13) Wampfler et al. (2014); (15) Fontani et al. (2015) ; (16) Hermsen et al. (1986)

§ In each N_2H^+ entry the uppermost value is for the $^{15}NNH^+$ isotopologue. # Larger value is a lower limit. † This range can be taken as a surrogate for the HCN ratio, however in comets there may be additional sources of CN (see Mumma & Charnley 2011). Only 2 measurements have been made for in HCN itself, in OC comets Hale-Bopp and 17P/Holmes. ‡ 'Average' based on optical observations of NH_3 daughter molecule NH_2 in an ensemble of comets.

Adapted from Wirstroem et al. (2016)

To test theoretical models of nirtrogen fractionation, we have also conducted observations towards 10 select dense cloud cores (Milam & Charnley 2012; Adande et al. 2018, in preparation). For example, Furuya & Aikawa (2018) recently proposed a model in which dense cores underwent isotope-selective photodissociation during an earlier diffuse phase, followed by ice formation during the dense phase. This model can explain the large observed N_2H^+ depletions (~1000, compared to a nominal ISM vale of 400) and predicts that ammonia should be much more enriched in interstellar ices. Thus, ice sublimation in protostellar cores should lead to observed ammonia fractionation ratios being much lower than in cold cores.

Figure 4 shows our spectra obtained towards two adjacent cores in L1262, one starless (L1262-core) and one containing a Class I protostar (L1262-YSO). The derived $^{14}NH_3/^{15}NH_3$ ratio from our observations (see Table 1) shows that the protostar is in fact more depleted in ^{15}N than the starless core, allowing us to rule out the model of Furuya & Aikawa.

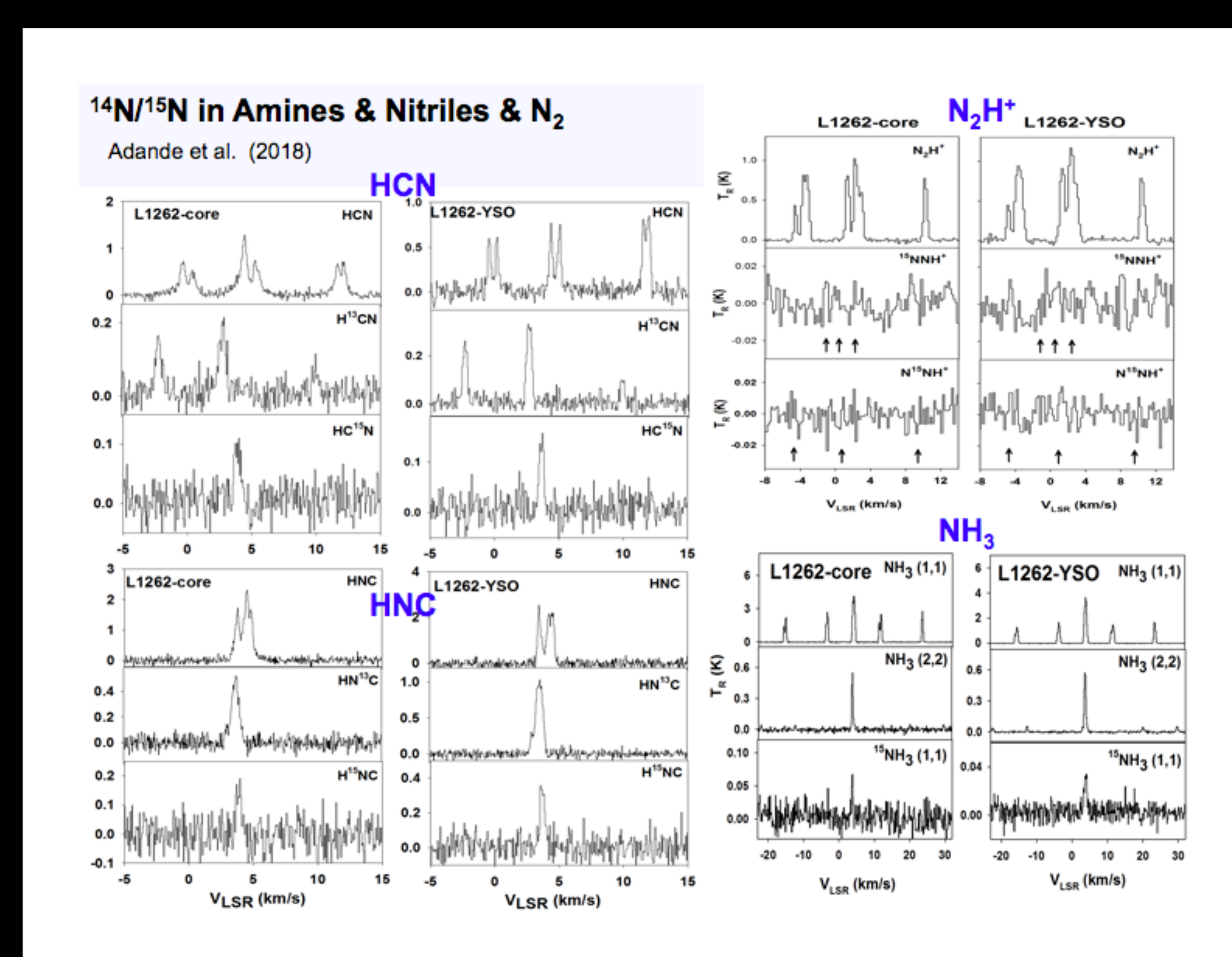

Figure 4. *Left panel*: Onsala Space Observatory and Green Bank Observatory spectra of molecules and their isotopologues in starless core L1262-core and the protostellar core L1262-YSO (Adande et al. 2018, in preparation).

Summary

Interstellar fractionation chemistry can potentially explain the range of D and ^{15}N enrichments found in primitive matter. A combination of theory and observation is essential to provide insight into the viability of elementary fractionation processes and test astrochemical models. The current status of ^{15}N fractionation indicates that there are still theoretical aspects that are not fully understood. New quantum chemistry calculations and laboratory studies of ion-molecule and neutral processes are urgently needed.

Aleon, J. 2010, ApJ, 722, 1342
Charnley, S.B., Rodgers, S.D. 2002, ApJ, 569, L133
Furuya, K. & Aikawa, Y. 2018, ApJ, 857, 105
Lauretta, D.S. and McSween, H. Y. Jr. (eds.) 2006, *Meteorites and the Early Solar System II*, University of Arizona Press, Tucson
Milam, S.N., Charnley, S.B. 2012, LPSC Abstracts, 43, 2618
Mumma, M.J., Charnley, S.B. 2011, ARAA, 49, 471
Pagani, L. et al. 2011, ApJ, 739, L35
Rodgers S.D., Charnley S.B., 2008, ApJ, 689, 1448
Roueff, E. et al. 2015, A&A, 576, , A99
Wirström, E.S. et al. 2012, ApJ, 757, L11
Wirström, E.S. et al. 2016, IAU Focus Meeting, 29, 271
Wirström, E.S. & Charnley, S.B. 2018, MNRAS, 474, 3720

This work was supported by the NPP, NASA's Emerging Worlds Program.and by FLaRe.