NITROGEN SUPERFRACTIONATION IN INTERSTELLAR CHEMISTRY. S.B. Charnley, S.D. Rodgers, *Space Science & Astrobiology Division, MS 245-3, NASA Ames Research Center, Moffett Field, CA 94035, USA (charnley@dusty.arc.nasa.gov; rodgers@dusty.arc.nasa.gov).*

Introduction Laboratory analyses of primitive solar system materials, such as meteorites, interplanetary dust particles (IDPs), and cometary dust particles returned by the *Stardust* mission, show anomalous fractionation in the heavy isotopes of numerous elements relative to that expected from the cosmic or solar system values [1-4]. In the case of hydrogen and nitrogen, the large D/H and ^{15}N/^{14}N ratios observed in some phases have been attributed to the survival of D- and ^{15}N-enriched material from the interstellar medium (ISM) [5,6]. For deuterium, the observed ratios are consistent with models and observations of the ISM, where low-temperature ion-molecule reactions lead to enhanced D/H ratios in both gas- and solid-phase species [7,8]. However, there is little observational data on nitrogen isotope ratios in the ISM, and models of the ^{15}N fractionation in typical dense clouds predict modest enhancements of ~ 25 per cent [9]. In comparison, the largest ^{15}N enhancements detected in meteorites – in so-called 'hotspots' – have ^{15}N/^{14}N enhancements of more than a factor of four relative to the Earth (i.e. $\delta^{15}\mathrm{N} > 3000$ ‰) [10] Values of $\delta^{15}\mathrm{N} > 1000$ ‰ have also been found in hotspots in IDPs and *Stardust* samples [11,12,4].

Interstellar Chemistry We previously demonstrated that significantly increased ^{15}N fractionation can occur in molecular clouds when CO is depleted onto dust grains but N_2 is not [13].Ion-molecule reactions at low temperatures preferentially drive ^{15}N into molecular nitrogen at the expense of atomic N^0 which becomes isotopically light. Under normal dark cloud conditions the degree of fractionation is limited by chemical reactions involving OH which cycle nitrogen between atomic and molecular form. However, if CO is frozen out as ice, OH is unavailable, this cycle is broken, and much larger ^{15}N-enhancements are possible.

This model could account for the presence of high bulk δ^{15}N values in IDPs [6], and was also able to account for the non-detection of N_2 in comets. Some additional processing was indicated to incorporate the ^{15}N-enriched ammonia into the carbonaceous matter, and secondary energetic processing to add $^{15}NH_2$ side-groups to polycyclic aromatic hydrocarbon (PAH) molecules was suggested. However, the model was unable to reproduce the largest δ^{15}N values seen in the hotspots. Moreover, the experimental determination by Geppert et al. [14] that recombination of N_2H^+ preferentially breaks the N≡N bond, producing N^0 and NH, acts to suppress the maximum fractionation [15].

We have been motivated to revisit our previous models as a result of several recent discoveries. Firstly, the experimental results in [14] have been challenged by Molek et al. [16], who demonstrated that recombination of N_2H^+ leads predominantly to N_2+H, as indicated in previous work [17]. The new results indicate that rupture of the N_2 bond occurs rarely, if at all, with an upper limit for the NH + N^0 branching ratio of 5 per cent. Secondly, observations of several pre-stellar cores have revealed that they have temperatures below 10 K in their central, densest regions. For example, $T = 5.5$ K in L1544 [18], and $T = 7$ K in L134N [19]. Due to the small zero-point energy differences involved, ^{15}N fractionation chemistry is extremely sensitive to temperature, and these lower temperatures may be expected to yield larger ^{15}N/^{14}N ratios. Thirdly, observations of N_2H^+ in dark clouds imply N_2/H_2 abundances of a few $\times 10^{-6}$ [20] This is significantly less than the galactic elemental nitrogen abundance, Maret et al. proposed that the 'missing' nitrogen was in atomic form and that the high inferred N^0/N_2 ratios could affect ^{15}N fractionation. Finally, in our earlier work we only calculated the bulk isotope ratios in the ammonia ice. In reality, the grain mantles will have an 'onion-ring'-like structure consisting of sequentially accreted monolayers. Thus, temporal variations in the gas-phase ^{15}N/^{14}N ratios will be preserved as spatial gradients in the ices, with each layer recording the gas-phase ratio at the time it was accreted. In particular, the late-accreting, uppermost layers will be the most highly fractionated. As it is these layers which are likely to experience the largest degree of subsequent processing, it is necessary to distinguish between the bulk isotope ratios in the ice as a whole, and those in specific monolayers.

Summary We have revisited our earlier work on ^{15}N fractionation based on recent experimental and observation results. Using the branching ratios for N_2H^+ dissociative recombination derived in [16], we effectively recover the results of our earlier work in dense, CO-depleted gas at 10 K. We have investigated the effects of varying the temperature, and show that at lower temperatures, larger ^{15}N/^{14}N ratios are produced in gas-phase in N_2. However, the barrier for the reaction of N^+ ions with H_2 sets a lower limit on the temperature at which ammonia can be produced efficiently. Assuming the 'standard' rate coefficient for this reaction we find that very little ammonia ice is generated for $T < 7$ K. We have also looked at the effects of a substantial N^0/N_2 ratio at $t = 0$. We find that, because roughly half of the initial N_2 ends up in the form of NH_3 and NH_2, reduced molecular nitrogen abundances yield less ammonia ice in total. Smaller N^0/N_2 ratios do not significantly affect the peak gas-phase fractionation ratios, but because the highly-fractionated ammonia formed at late times represents a greater proportion of the total ice, we find that the bulk ice ^{15}N/^{14}N ratio can be greatly increased.

Following the ^{15}N/^{14}N ratios in individual monolayers as they accrete sequentially from the gas, we find that gas-phase temporal variations in isotopic ratios are preserved as spatial gradients in the layered ammonia ice. The uppermost layers which accrete at late times have the largest ^{15}N-enhancements, up to an order of magnitude with respect to the elemental ^{15}N/^{14}N ratio (see Figure 1). Converting to δ-values to compare with laboratory determinations, we derive peak values of $\delta^{15}N > 3000$ ‰ in gas at 10 K, with larger values occurring

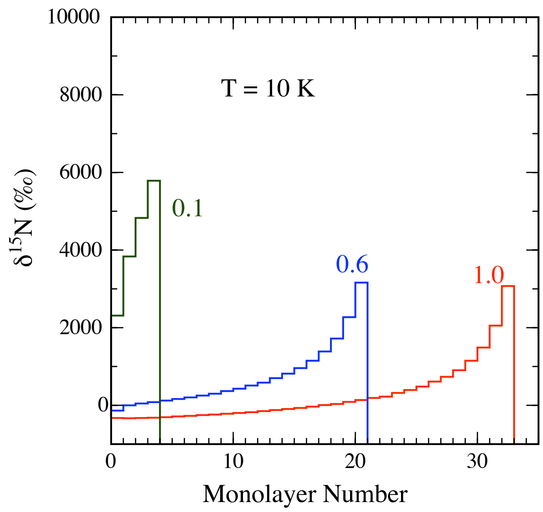

Figure 1: δ^{15}N values in different ammonia monolayers for $T = 10$ K . Labels refer to the fraction of nitrogen initially assumed to be molecular.

in models with slightly lower temperatures and smaller N^0/N_2 ratios. This is more than sufficient to account for the largest measured hotspot ratios, and demonstrates that interstellar gas-phase chemistry is likely the source of cometary and meteoritic ^{15}N anomalies.

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