NITROGEN ISOTOPIC FRACTIONATION IN VUV PHOTODISSOCIATION OF N$_2$: IMPLICATIONS FOR THE EARLY SOLAR SYSTEM.

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Introduction: Laboratory analyses of primitive solar system materials, such as meteorites, interplanetary dust particles (IDPs) and cometary dust particles returned by the *Stardust* mission, exhibit anomalous fractionation in the heavy isotopes of numerous elements relative to that expected from the cosmic or solar system values [1-4]. These findings challenge our understanding of the formation and evolutionary history of the solar system.

Nitrogen chemistry is particularly interesting. The isotopic ratio (^{15}N/^{14}N) has been measured in a variety of solar system bodies, from the giant planets to the rocky planets, comets, and meteorites. Figure 1 shows the nitrogen isotopic composition of different solar system objects [5].
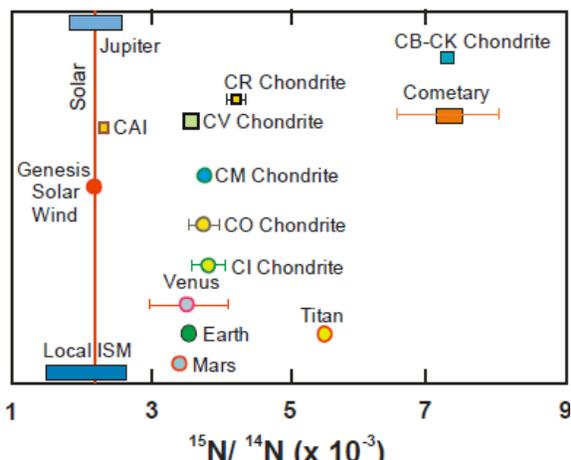

Figure 1. Nitrogen isotopic composition of different solar system objects. Solar wind composition measured through Genesis samples is also shown (data taken from [5], reproduced from [6]).

The most abundant nitrogen bearing components in carbonaceous chondrites is organic matter [7]. Until now, the most extreme enrichments in ^{15}N have been found in 'hotspots' (regions that are extremely isotopically enriched relative to the surrounding matter) in anhydrous cluster IDPs. The largest ^{15}N enhancements detected in meteorite 'hotspots' have ^{15}N/^{14}N enhancements of more than a factor of ~5 relative to the Earth (i.e. δ^{15}N>4000‰ [8]. Values up to 1500 ‰ have been observed in whole rock carbonaceous chondrites [9] and ~ 1000 ‰ have also been found in hotspots in IDPs and *Stardust* samples. In

contrast, IOM (interstellar organic matter) from meteorites, whose parent bodies are in the asteroid belt, display bulk isotope anomalies that are relatively small compared to those in IDP hotspots [10].

The ^{15}N excess relative to the Earth's atmospheric value indicates that N-bearing volatiles in the solar nebula underwent important N isotopic fractionation at some stage of solar system formation. The N-isotopic composition in the Jovian planet and Titan have been modeled [11] and it was suggested that N$_2$ photolysis may explain the ^{15}N enrichment observed in HCN for Titan's atmosphere, whereas, for Jupiter's atmosphere, NH$_3$ photolysis was prescribed. However, the processes active within the solar nebula which potentially can modulate the isotopic composition of nitrogen are not clear and remain an open question. It is possible that self-shielding dominates N$_2$ photolysis and can play a leading role. The extreme range of isotopic variation observed in early solar system materials is interesting and requires mechanistic understanding. In this abstract, we present the first experimentally determined N-isotopic fractionations during VUV photolysis of N$_2$ using the ALS synchrotron.

Experimental: VUV photolysis of N$_2$ was carried out in a differentially pumped reaction chamber described earlier [12]. The trapping of the product N-atoms is nontrivial. A steady flow of high purity premix gas (N$_2$: H$_2$ = 50 : 50) was established in the reaction chamber at a pressure of 200 mtorr (column density ~ 4 x 10^{17} molecule/cm^2). Photolysis of this gas mixture was carried out at six different synchrotron bands (86 to 98 nm, FWHM = 2.2 nm) in six different experiments while keeping the column density constant. Photolytically produced atomic N was trapped as NH$_3$ and collected in sample tubes and analyzed at UCSD. Due to the lower gas phase rate constant of NH$_3$ formation reaction, the NH$_3$ yield was about 0.2 micromoles. N$_2$ was produced by pyrolyis (in presence of CuO) of NH$_3$ as described by [13]. Finally, N-isotopic composition of N$_2$ was measured using a Finnigan MAT 253 IRMS.

VUV photochemistry of N$_2$: The absorption bands of N$_2$ can be divided into two regimes; above 100 and below 100 nm. Above 100 nm, there are only a few absorption bands and below 100 nm there are several. Predissociation of N$_2$ is well known through photons of < 100 nm [14] and is a good candidate for studying

isotopologue selection. Since N_2 and CO are isoelectronic, there are many similarities in the spectra of these two molecules [15]. A large effect in oxygen isotope have been measured for the indirect (accidental) predissociative states of CO (e.,g., at 105.17 and 107.62 nm) [12]. Likewise, several states are indirectly predissociative for N_2. As an example, the $b^1\Pi$ state (accessible by 95.2 nm photons) indirectly predissociates via the $C^3\Pi$ state to the continuum of $C'^3\Pi$. A recent *ab-initio* theoretical study on isotope effects during photoexcitation of the N_2 molecule, displays a large isotope effect (thousands of permil) and is highly energy sensitive due to the coupling geometry of the potential energy surfaces [16].

Results and Discussion: The N-isotopic compositions measured for all six synchrotron bands are shown in Figure 2. The result shows that the fractionations are linearly dependent on wavelength. As the column densities are kept constant for all six experiments, the only variable is the wavelength. Since the synchrotron band is 2.2 nm wide, a number of N_2 absorption bands are included within every synchrotron band. A detail band-by-band analysis is being undertaken to better understand the results.

An isotope self-shielding calculation have been performed using an *ab-initio* approach: by taking the diabatic potentials from [17] with states b, c, o, b', c', e' (of Π and Σ symmetries) and adding triplet Π states F, G, C. C' with their spin-orbit coupling to the singlets, a total 342 bound vibronic states in the Hamiltonian is obtained. The Hamiltonian is diagonalized to generate an adiabatic spectrum of the molecule, which shows good agreement with the experimental results [18]. This process was performed separately for three isotopologues (14-14, 14-15, and 15-15). Total absorption of each isotopologue was calculated incorporating the calculated cross-sections and experimental parameters using the Beer-Lambert law. The calculated isotope ratios are normalized to air isotope ratio to calculate δ-values (shown in blue in Figure 2).

Figure 2 shows the comparison between the measured isotopic fractionation to that expected from self-shielding. The measured values do not match the calculated ones (except at one lower wavelength data point) and indicate additional fractionations in predissociation process, over and beyond the fractionation due to isotope self-shielding.

Regarding the mechanism for the measured isotopic fractionation, a crucial point is that VUV photodissociation is a potential mechanism in the solar nebula to generate unprecedented isotopic fractionation observed in IDP hotspots and IOM's. Moreover, in the present experiment, the N-isotopic enrichments are stored in NH_3, which represents a direct analog to the

solar system. The enriched nitrogen could be trapped in NH_3 and serve as a precursor of the organic molecules as observed in IOMs.

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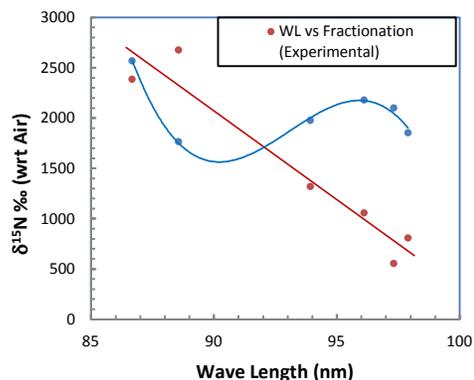

Figure 2. *N-isotopic fractionations in VUV photo-dissociation of N_2. Red: measured value using ALS synchrotron. Blue: calculated value using isotope self-shielding approach using the cross-sections calculated by ab-initio method (see text for detail).*