ARE ORGANIC MACROMOLECULES IN METEORITES FORMED WITHIN THE SOLAR SYSTEM?
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Introduction: Nitrogen is a vital element for life on Earth because it is a basic ingredient of amino acids that constitute all nucleic acids and proteins. Nitrogen isotopic analyses ($^{15}$N/$^{14}$N) of solar system objects (e.g., meteorites, terrestrial planets, atmospheres of giant planets and their moons, solar wind, comets and interplanetary dust particles (IDPs) \cite{1} and references therein) advance understanding of prebiotic processes and defining the volatile inventory of the solar nebula. Bulk meteorite analysis exhibit a variation in the range of few hundred permil in $\delta^{15}$N (wrt to air-N$_2$) \cite{2-4} with occasional exceptionally high values (as well as range of variation) in some carbonaceous chondrites, stony-iron and, iron meteorites (Figure 1A). The N-isotopic composition measured in a returned Solar wind sample from the Genesis discovery mission and in the atmosphere of Jupiter (in N$_2$H$_4$) are nearly equally depleted ($\sim$ - 400‰, \cite{5, 6}. Conversely, extremely high $^{15}$N enrichments are observed as shown in Figure 1B in meteoritic ‘hotspots’ (of $\sim$5000‰ in some cases), interplanetary dust particles (IDPs), cometary samples (including that from Stardust mission) and, in insoluble organic matter (IOM) from meteorites \cite{7-9}.

High $^{15}$N enrichments are not always correlated with carbon isotopes (e.g., $^{13}$C/$^{12}$C) \cite{2-4, 10, 11}, though there are occasional correlations with high D/H ratios \cite{12}. The relationship of nitrogen with carbon and hydrogen is important because of their presence in nitrile (-CN) and amine (-NH$_2$) functional groups in organic molecules. The D/H enrichment in the interstellar medium has been modeled at low temperatures (25K), including ion-neutral reaction fractions \cite{13}. Models of ion-molecule exchange reactions at extremely cold temperatures for N-isotopes include formation of $^{15}$N enriched functional groups in interstellar clouds and it is possible to form amine group molecules with $^{15}$N enrichments of $\sim$3000‰ in this process \cite{14, 15}. The uncertainties of these models largely resides in the unknown rate coefficients of key exchange reactions as there are a few experimental measurements and the theory of ion-molecule fractionations are not well worked out \cite{14}. Ion-neutral exchange reaction models predict simultaneous D and $^{15}$N enrichments, however, the lack of correlation between these two isotopic systems in the solar system weakens the premise that D and $^{15}$N enrichments are purely of presolar origin \cite{12}. A recent model predicts uncorrelated D and $^{15}$N enrichments and includes ortho and para forms of nitrogen in an ion-molecular reaction network \cite{16}. Processing of nitrogen through isotopologue selective photodissociation (i.e., isotope self-shielding) in the vacuum ultra violet (VUV) wavelengths has been proposed \cite{17}. In this abstract, we present wavelength, temperature and, pressure dependent N-isotopic fractionations during VUV photolysis of N$_2$ and discuss the relevance to the solar system.

Experimental: VUV photolysis of N$_2$ was carried out in a newly built, differentially pumped reaction chamber similar to the one described in \cite{18}. The trapping of the product N-atoms is non-trivial. A steady flow of high purity premixed gas (N$_2$: H$_2$ = 50 : 50) was established in the reaction chamber at two different N$_2$-partial pressures of 62 and, 100 mtorr, respectively, in three sets of experiments (range of column density: 3 - 5 x 10$^{17}$ molecule/cm$^2$). Photolysis of this gas mixture was carried out at ten different synchrotron bands (80 to 98 nm) at two different temperatures (23 and -78°C) in three sets of experiments. Photolytically produced atomic N was trapped as NH$_3$ and collected in sample tubes. Due to the lower gas phase rate constant of NH$_3$ formation reaction, the NH$_3$ yield was low ($\sim$ 0.1 to 1.3 micromoles. N$_2$ was produced by pyrolysis (with CuO) of NH$_3$ and N-isotopic composition was measured using a Finnigan MAT 253 IRMS.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{Figure1.png}
\caption{N-isotopic compositions of different solar system objects-(A) bulk analysis, (B) phase-specific micro-analysis.}
\end{figure}
**Results:** The measured N-isotopic enrichment profiles across the wavelengths for three different sets of experiments are shown in Figure 2. Unprecedented $^{15}$N enrichment is observed at a wavelength of 90 nm (111111 cm$^{-1}$). This particular wavelength zone is quite unique because of extensive state mixing in highly localized spectral regions (inset diagram of Figure 2) leading to large scale perturbations.

![Figure 2. Measured and calculated wavelength dependent N-isotopic enrichment profiles. Inset diagram shows the computed absorption cross-section of $^{14}$N$_2$ and $^{14}$N$^{15}$N near the peak (90 nm) reflecting extensive state mixing.](2452.pdf)

VUV photochemistry of N$_2$: N$_2$ absorbs photons through slightly broadened partly overlapping rovibrational lines in the VUV region and dissociates via a repulsive triplet state. The absorption is subject to shielding primarily by absorption of the more abundant $^1$N$_2$ isotopologue resulting in an enrichment of $^{15}$N in the dissociation product due to preferential absorption of rarer $^{14}$N$^{15}$N and $^{15}$N$^{15}$N isotopologues [17]. Isotopic fractionation based on self-shielding was calculated for the present experiments using cross-sections from [19], which show higher enrichments compared to the experiments (Figure 2). The computed profile also shows a significant dependence on density suggesting self-shielding is a significant consideration but more importantly an additional and massive isotope effect must be considered to explain the unprecedented enrichment peak at 90 nm.

**Connection to the Solar Nebula:** Aromatic molecules (polycyclic aromatic hydrocarbons, PAHs) are the most common class of organic compounds in the universe in gas-phase as well as in carbonaceous dust [20, 21]. The IOMs are consisting of an aromatic condensed core, connected by aliphatic and ether linkages with various functional groups attached. When nitrogen replaces a carbon in the ring structure, it forms polycyclic aromatic nitrogen heterocycles (PANHs), the nucleobases, the essential building block for the origin of life and a prebiotically significant component. PANHs are possibly formed in the cold molecular cloud; however, these species are not resistant to UV and have a short life time of ~12 hours in extreme environments [20]. Nitrogenation of PAHs is possible while frozen in ice along with nitrile and amine functional groups while exposed to UV [22]. The PANHs could probably form inside the solar system by nitrogenation of PAHs and have not likely been transported from elsewhere. Production of a highly enriched $^{15}$N atom from N$_2$ photodissociation as demonstrated in the present experiment at the outer edges of the disk with subsequent production of $^{15}$N enriched amine and nitrile group molecules is plausible. Once formed, these functional groups may freeze-out in the ice and possibly synthesize PANHs within the ice with high $^{15}$N enrichment under UV exposure [20, 22, 23].

The range in observed nitrogen isotopic compositions extends to ~5000‰; thus a process(es) of this magnitude is needed to account for observations. The present experiments show that at selected wavelengths, nitrogen photolytic effects are more than double this range (12,000‰, Figure 2).

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**References:**