THE PECULIAR NATURE OF NITROGEN IN ORGANIC SOLIDS FROM CHONDRITIC METEORITES.  G. D. Cody¹ and C. M. O’D. Alexander², ¹Geophysical Laboratory. Carnegie Science (gcody@carnegiescience.edu), ²DTM, Carnegie Science (calexander@carnegiescience.edu).

Introduction: Insoluble organic matter isolated from the matrix of carbonaceous chondrites contains appreciable nitrogen (~ 3-4 N’s per 100 C’s [1]). As this nitrogen resides in a complex amorphous organic macromolecule it is clear that a solid state spectroscopy, sensitive to N bonding environments, would be required to learn about N in IOM at the functional group level. The two obvious spectroscopies are ¹⁵N Solid State Nuclear Magnetic Resonance (SS-NMR) and N X-ray Absorption Near Edge Structure (XANES) spectroscopy.

¹⁵N SS-NMR: Such analyses typically employ ¹H-¹⁵N cross polarization that vastly improves S/N usually making the detection of nitrogen at the concentrations present in IOM very straightforward. We have attempted three times to obtain ¹⁵N SS-NMR spectra using large samples ~ 80 mg, employing considerable acquisition time and have not detected any signal. IOM samples analyzed included Murchison CM2 (N at.% = 3.3, δ N¹⁵=1 %), GRO95577 CR2 (N at. % = 3.2, δ N¹⁵=+233 %), and Tagish Lake C2 (N at. % = 4.3, δ N¹⁵=+73) [1]. One other study has also employed ¹⁵N SS-NMR focusing on Murchison and Orgueil IOM [2]; in that study a low S/N ¹⁵N SS-NMR spectrum was obtained for Orgueil IOM, where the major signal was attributed to pyrrolic N (R-NH-R), but no signal was obtained for Murchison, consistent with our results. It must be noted that every NMR experiment is “tuned” up with known standards, so a lack of detection is not a failure of NMR, rather it means that the “sample” differs from the “standard” in some significant way. So we find that out of four robust attempts to obtain ¹⁵N SS-NMR on IOM, we have three failures to detect signal and one low S/N (“low” meaning lower than what standards would predict) spectrum.

N-XANES: Whereas ¹⁵N SS-NMR signal acquisition is complex and can be compromised, in any one of a number of ways, N-XANES is a very straightforward analysis- monochromatic X-ray light is absorbed based on excitation of direct electronic transitions to various bound states (in the near Edge region), a continuum absorption above the ionization edge (proportional to N content), and photo-electron scattering related to local atomic structure (EXAFS- on top of the atomic absorption cross section). However, extracting quantitative N functional group abundances from N-XANES is much more difficult than from ¹⁵N SS-NMR spectra.

Fig 1: N-XANES data of primary (2H), secondary (1H) and tertiary (0H) amines in model compounds from the N K edge spectra of model compounds [3]. Note that pre-edge feature at ~ 402 had intensity proportional to the # of H’s bonded to N, whereas the continuum absorption at energies > 430 eV are the same.

In order to “fit” N-XANES spectra one has to fit all regions of the spectrum. So one must fit not just the pre-edge features, i.e., those peaks at the lowest energies, but also, one must constrain the fit with the the atomic absorption cross section, the “K-edge” that dominates absorption at high energies. An example of this is shown in Fig. 1, where three N-XANES spectra are shown for variously substituted simple “amine” molecules are presented [3]; depending on the hydrogen content the intensity of the pre-edge feature (~ 402 eV) varies enormously, whereas ionization cross section absorption is independent of this, being proportional only to the number density of N- atoms in the cross section of the X-ray beam. This is a general feature of XANES.

Acknowledging this complexity, we have set out to fit the N-XANES spectrum of IOM (in this case Tagish Lake as being representative of most IOM), using a range of model spectra as presented in the EELS spectral data base [3].

Our partial fit is presented in Fig. 2 where we can account for ~ 80 % of the total absorption intensity through a combination of model imine, nitrile, amine,
pyrrole N (1s) spectra. The remaining “unaccounted” region of the near edge region is at high energy for typical N-XANES and we could only find one possible candidate to explain this absorption. Bear in mind that in the case of C-, N-, and O-XANES the primary cause of shifts to higher excitation energy is the electron withdrawing tendencies of nearest neighbor atoms.

Fig 2. Tagish Lake IOM N-XANES spectrum (Blue) and a best fit of multiple N-XANES full spectral standards (Red). Note that this fit only accounts for ~20 at. % of the N, a significant high frequency component remains unaccounted for.

As is the case for carbon and sulfur, nitrogen when bonded to oxygen (a very electronegative neighbor) the 1s electron binding energies increased, such that any core level transitions are shifted to higher energies. The gap in our fit (Fig. 2) is consistent with N bonded to oxygen as in nitro groups. Exemplified by a N-XANES spectrum of a simple nitro compound-nitrobenzene [3]; see the difference spectrum in Fig. 3.

So if we accept our fit (Fig 2) and our assessment of the unaccounted for N being in the form of oxygenated N (e.g. R-NO₂) we end up concluding that N speciation is as follows: ~ 3 % imine, ~ 4 % nitrile, ~ 12 % pyrrole, ~ 0 % primary amine, ~ 30 % secondary amine (N-H), ~ 30 % tertiary amine (N), and ~ 21 % nitro (NO₂) groups. We further note that nitrile at near 400 eV can overlap with certain imines (e.g. imidazole imine [3]), so we can not really say that there is definitively any nitrile in IOM. Note that nitrile is one of the most reactive functional groups to aqueous chemistry [4]; therefore, it is more likely than not that there is not even 4 % nitrile in IOM; rather this Nitrogen as observed in N-XANES is actually not nitrile but rather imidazolic imine [3].

^{15}N Isotopic enrichments and ^{15}N Hotspots: Considerable attention has been placed on the nature of ^{15}N enrichments in IOM, for example between CM’s Murchison (-1 ‰) and Bells (+415 ‰). Conventional wisdom is that enrichments in ^{15}N (as is also the case for ^{2}H) are signals of inherited interstellar chemistry. However, N-XANES spectra of Murchison and Bells (not shown here) are essentially identical as are their ^{13}C SS-NMR spectra. The analysis presented here strongly supports the idea that the initial source of N was ammonia, most likely interstellar in origin. It is, therefore, reasonable to expect that the source of the variation in ^{15}N enrichment is variation of the ^{15}N abundance of ammonia, either during the point of IOM synthesis or perhaps modified by subsequent nitrogen exchange through amination/de-amination equilibria.

Fig 3. The difference between the Tagish Lake N-XANES spectrum and the partial fit (see Fig. 2) where it is seen the majorit of residual lies in a pre-edge peak centered at 403.5 eV that is coincident with N in the form of nitro groups (R-NO₂) [3].

Finally, the presence of substantial nitro (NO₂) groups indicates that at some time after incorporation into IOM, exposure to strong oxidants converted a fraction of the amino groups to nitro groups [4]. This would have undoubtedly occurred in an aqueous media requiring that this chemistry occurred in the interiors of planetesimals. The identity of the oxidant is not known, however, it has been suggested previously, that radiolysis of water is expected to lead to the formation of hydrogen peroxide, super oxide and O3 [5].

References: