SOLID STATE NUCLEAR MAGNETIC RESONANCE STUDIES OF THE MURCHISON ORGANIC MACROMOLECULE. G. D. Cody III, C. M. O D. Alexander, F. Tera S. Carnegie Institution of Washington, 5251 Broad Branch Road NW, Washington, DC 20001. <cody@gl.ciw.edu>

We continue to explore the macromolecular structure of the Murchison Macromolecule using non-destructive spectroscopic techniques (see 1 and 2). In this abstract we present the results of experiments designed to separate the contributions of protonated vs non protonated carbon, a crucial distribution for the development of statistical molecular models of macromolecular solids.

Results: In order to separate the contributions of protonated vs non-protonated carbon we have exploited relatively slow spinning (4 kHz at the Magic Angle) with variable amplitude cross polarization at relatively high field (~75 Mhz $^{13}$C and ~ 300 Mhz $^1$H). The slow spinning ensures that remains substantial heteronuclear coupling between carbon and protons. The method of cross polarization exploits the transfer of spin polarization from an abundant proton spin reservoir to a dilute spin ($^{13}$C) reservoir. There is, therefore, a reasonable question as to whether all carbons, particularly those not directly protonated, will receive the same degree of polarization transfer. Substituted aromatics and polycyclic aromatic compounds in particular may be subject to incomplete cross-polarization. Rapid diffusion of spin polarization across the proton spin system may serve to evenly distribute polarization among variously protonated carbons, however it cannot compensate for significant distance from a proton. We tested our particular VACP experiment for quantitation on a number of compounds including hexamethylbenzene, vanillic acid, 2,6 dimethylnaphthalene, and chrysene. In each case, the peak intensities were within 2 % of the expected values indicating that carbons one atom away from a proton are polarized to nearly the same extent as directly protonated carbons. However, with very large PAH systems, carbons buried within the molecule (2, 3, or more carbons away from a proton) may receive less polarization. Indeed our estimates of the H/C and O/C ratio derived from the CP MAS results presented in Figure 2 and Table 1 were more than a factor of two higher than the actual values obtained from elemental analysis. This suggested that the CPMAS was accounting for less than half the carbon.

The spectrum in figure 1 will reveal all carbon within two bonds of hydrogen. It is acknowledged that larger carbonaceous domains may not contribute to the spectrum. Note that the highly anisotropic nature of aromatic carbon lends itself to the generation of significant spinning sideband intensity evident by the peaks at ~ 183 ppm, 236 ppm, and ~ 75 ppm.

![Figure 1: VACP 13C-1H MAS experiment (4 Khz) spinning speed and high power (75 Khz) proton decoupling.](image1)

![Figure 2: VACP 13C-1H MAS experiment (4 Khz) spinning speed and no high power (75 Khz) proton decoupling. Note that the CH$_3$ group is a small peak on an intense spinning side band.](image2)
Solid State NMR of the Murchison Macromolecule: G. D. Cody et al.

with CH$_3$ groups. Integration of the spectrum in figure 2 reveals that ~3% of the signal results from CH$_3$.

Figure 3: Subtraction of the two spectra reveals the protonated carbon, aromatic C-H, and methine and methylene.

Deconvolution of the difference spectrum presented in Figure 3 reveals that ~40% of the intensity is from aromatic carbon and ~60% is from aliphatic carbon.

In addition to carbon we have also explored proton NMR. Advances in NMR hardware and theory over the past couple of decades now make it possible to acquire solid state proton NMR, data that would clearly complement the aforementioned carbon data. The beauty of proton NMR lies in the enormous natural abundance of $^1$H as well as the intrinsic sensitivity of the nucleus (second only to tritium). By far the easiest element to detect using NMR is hydrogen. Unfortunately, the problem with $^1$H solid state NMR is also related to the abundance of protons, i.e. the very strong dipolar interactions between them inevitably lead to intense broadening of resonances obliterating spectral information. With larger samples one can apply methods such as combined rotation and multi-pulse excitation methods (CRAMPS). We are in the process of obtaining these data on the same sample used for carbon SP MAS (Figure 2). For extremely small samples, however, we have resorted to a brute force approach, i.e. if one spins a sample fast enough one can average much of the dipolar interactions to near zero and achieve a relatively well resolved proton spectrum. Using an ultra-fast MAS probe capable of nearly 2,000,000 RPM sample spinning we have obtained what we believe to be the first solid state proton spectrum of meteoritic organics.

Figure 4: High speed MAS $^1$H multi-pulse spectrum (DEPTH was used for background suppression)

Analysis of the $^1$H spectrum indicated that ~40 of the protons are aromatic and ~60% are aliphatic. Consistent with an abundance of methine over methylene and methyl groups.

Conclusions: These results provide critical constraint towards the development of a macromolecular model for the structure of the Murchison organic Macromolecule. When combined with the previous results obtained at high spinning speeds (1 and 2), a picture begins to emerge of a highly cross-linked macromolecular system.

Acknowledgments: The Authors gratefully acknowledge financial support from NASA’s Origins of the Solar System program.

References: