Introduction:

A critical aspect of characterizing the diagenetic evolution of organic macromolecules is the ability to unambiguously extract structural information from molecular spectroscopic analyses. Towards this end, we have been applying ab initio calculations (e.g. Density Functional Theory) to determine molecular spectroscopic characteristics, e.g. $^{13}$C chemical shielding and Carbon X-ray absorption Near Edge spectroscopy, related to macromolecular structure. In all cases geometry optimization of molecular fragments representative of the macromolecules were carried out using Density Functional Theory employing the generalized gradient approximation. NMR shielding calculations employ the Individual Gauge for Localized Orbital Method and were used to assess whether inhomogeneous spectral broadening due to both functional group variation and local configurational variability may inhibit the detection of otherwise significant quantities of alkyl-aryl ethers in lignin derived geopolymers.

Determination of the chemical shielding tensor principal axis values are shown to reveal a strong correlation between anisotropy and asymmetry with local configuration effects such as dihedral rotation angle, phenyl group rotation, and bond angle variation.

Computational chemistry has also been applied to calculate C-XANES spectra and have proven to be essential for the assignment of certain spectroscopic characteristics observed to be present in kerogens (geopolymers) that correlate with diagenesis. Specifically, extended Hückel molecular orbital calculations (EHMO) were performed on acetic acid, benzeneacetic acid, benzene, and benzoic acid, focusing on electronic coupling effects on the generation of higher order $1s-\pi^*$ transitions. The effects of core level photoexcitation of the carboxyl carbon were simulated using the equivalent ionic core virtual orbital model (EICVOM).

The methodology derived to allow for spectral deconvolution of organic solids has also been used for the study of other complex amorphous solids of geochemical relevance-silicate glasses. Specifically, an investigation of the structure of sodium aluminum silicate glasses (composition: $(x)Na_2O, (1-x)Al_2O_3, 0.9SiO_2$ perturbed through the addition of 2 mol % $P_2O_5$) was performed using a combination of $^{27}$Al, $^{29}$Si, and $^{31}$P solid state NMR spectroscopy and ab initio chemical shielding calculations (GIAO method). Deconvolution of the $^{31}$P MAS NMR data using the results of the ab initio calculations (specifically the magnitude of the chemical shielding anisotropy $\delta_{11} - \delta_{33}$ and the computed isotropic chemical shifts $\delta_{iso}$ as a constraint), revealed that a minimum of 13 different phosphorous species must be present in these glasses over the compositional range investigated. It was concluded that the addition of even a small amount of $P_2O_5$ (2 mol %) results in a large perturbation of the structure of silicate glasses and should manifest significant effects in the physical properties of melts derived from them.

In general, wherever molecular spectroscopic techniques are used to derive structural information regarding amorphous solids, computational chemistry must also be used to constrain structural interpretation. An integrated approach of both experiment and theory provides.