

FUNCTIONAL GROUPS QUANTIFICATION OF CHONDRITIC ORGANICS BY XANES SPECTROSCOPY

C. Le Guillou¹ and S. Bernard², ¹UMET, CNRS UMR8207, Univ. Lille1, France, corentin.san@gmail.com
²IMPMC, CNRS UMR7590, Sorbonne Universités, MNHN, UPMC, IRD, Paris, France, sbernard@mnhn.fr

Introduction: X-ray absorption near edge structure (XANES) at the Carbon K-edge allows to study the origin and evolution of organic matter (OM) in carbonaceous chondrites by revealing the nature of the molecules, their diversity and their modifications during parent body processes [1, 2]. Different functional groups are expressed at different energies, and aromatics, ketones, or aliphatics can thus be identified. So far, it has been mainly used to attest of the presence/absence of a given function and to compare, based on absorption intensities, the relative abundance of a given functional group in different samples [1]. However, these comparisons remained qualitative because the absorption oscillator strengths (the probability for an X-ray to trigger an electronic transition) are unknown. Here, we report the development of a calibration based on reference materials and coupled to a data treatment process that aims at quantifying the absolute functional group concentration (aromaticity, aliphaticity, etc.). The spatial resolution of Scanning Transmission X-ray Microscopy (STXM) allows to do so with a probe size of 30 nm. It is then applied to chondritic organics previously measured *in situ* within FIB sections extracted from the matrices of various carbonaceous chondrites (CI, CMs, CRs). Two types of signature were recognized, one associated to sub-micrometric particles, and showing a higher aromaticity and another, occurring at a much smaller scale intimately embedded within fine grained silicates, which was less aromatic and more carboxylic-rich. Their molecular compositions obtained with the present method are presented.

Method: The XANES spectra of ten reference polymers covering a wide range of aromatic and aliphatic carbon concentrations were measured at the canadian light source and two additional published datasets available online (polymers and natural organic matter; [3, 4]) were analyzed as well (about 30 compounds in total). After a power law background subtraction, spectra are first normalized to the total amount of carbon in order to be accurately compared. We performed this normalization in a new fashion by integrating the spectra area between the pre-edge (280 eV for Carbon, 398 eV for Nitrogen) and the ionization energy (291.5 eV for C, 406.5 for N). The correlation obtained between the N/C_{measured} and the $N/C_{\text{reference}}$ is as good ($R^2 = 0.99$) as the one obtained by the classical method which consists of fitting absorption cross sections, confirming its validity. This new alternative normalization method is more accurate when spectra are acquired only up to 320 or 340 eV. Spectra were then fitted using ~ 20 Gaussians, set at given energies corresponding to functional group assigned in the literature, with a fixed FWHM of 0.4 eV. We also wrote a python program which automatically performs this suite of data treatments (background subtraction, N/C and O/C determination, normalization, fitting and output file writing) which will soon be made available online.

Results: We obtained good calibration curves between the known functional group concentration and their related absorption intensities: aromatic/olefinic carbon concentration correlates best with the sum of four gaussians placed at 284.4, 284.7, 285 and 285.4 eV ($R^2 = 0.98$); the sum of the concentration of ketones, phenol, and nitrile groups (which are not easily distinguishable) correlates best with the sum of three gaussians placed at 286.2, 286.5 and 286.8 eV ($R^2 = 0.94$); the aliphatics concentration correlate best with the sum of two Gaussians placed at 287.6 and 287.9 eV ($R^2 = 0.9$); and carboxylics and hydroxyls groups yield lower but reasonable calibrations ($R^2 = 0.77$ and 0.5) when using absorptions at 288.6 and 289.4 eV, respectively. Altogether, we demonstrate that it is possible to determine the absolute molecular composition of an unknown molecule/material using XANES (with about 15% to 40% accuracy depending on the functional group). Nuclear Magnetic Resonance (NMR) can also provides this type of quantification, but requires a much larger amount of material and do not offer the same spatial resolution.

Intriguingly, insoluble organic matter (IOM) in Murchison appears to have only about 35 % of its carbon present in aromatic/olefinic groups, a value significantly lower compared to previous NMR results ([5]; > 60%). Aliphatics represent, comparatively, a higher fraction than expected ($\sim 35\%$), whereas the ketone/phenol/nitrile groups represent $\sim 15\%$. The data obtained *in situ* from the FIB sections (Murchison and Paris CM chondrites, as well as weakly altered CRs) indicate a similar composition for the OM particles than the IOM (but a larger spread). In contrast, the diffuse OM found within silicates have a lower aromaticity (and a larger scatter than the particles) : in CRs, it is comprised between 20 and 30%, whereas in CMs it appears to be even lower, between 20 and 5%.

Altogether, this work offers an alternative approach to quantify the molecular composition of complex organic material, and thus allows to refine our understanding of organics in carbonaceous chondrites.

References: [1] Le Guillou et al. (2014), *Geochimica et Cosmochimica Acta* 131:368. [2] De Gregorio et al. (2013), *Meteoritics and Planetary Science* 48 :904 [3] Dhez et al. (2003), *Journal of Electron spectroscopy and related phenomena* 128:85. [4] Solomon et al. (2009), *Soil Science Society of America* 73:1817. [5] Gardinier et al. (2002), *Earth and planetary science letters* 184:9.